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# Clathrochelates

## Synthesis, Structure and Properties

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# Preface

Compounds with a metal ion encapsulated in a three-dimens ıl macropolycyclic ligand cavity have recently become of intense interest to scientists working in several fields of chemistry and biochemistry. This can be accounted for by the unique properties of the metal ion, completely caged by the macrobicyclic ligand and, to a great extent, isolated from environmental factors. Such complexes are suitable as membrane transporters, electron and ion carriers, models of metalloproteins and metalloenzymes, and other important biological systems (biomimetics), highly-selective and highly-sensitive analytical reagents, catalysts for photochemical and redox processes, cation and anion receptors, molecular electronic devices, and so forth.

Three-dimensional complexes with the encapsulated metal ion coordinating five or more nitrogen and/or sulphur donor atoms of not less than three macrocyclic fragments of an encapsulating ligand are named "clathrochelates." The concept of "clathrochelates" and this name itself were first proposed by D. H. Busch [1] and realized by D. R. Boston and N. J. Rose [2] for macrobicyclic cobalt(III) tris-dioximates. During the 30 years elapsed since the preparation of the first clathrochelates, several classes of such compounds (e.g., macrobicyclic tris-dioximates and tris-diiminates, sepulchrates, sarcophaginates and others), different in the capping groups, the degree of saturation, and the nature of the donor atoms, have been synthesized. Pathways of direct and directed synthesis of different types of clathrochelates, modification procedures for ligand peripheral groups, and cage framework modification reactions have been developed. The structure, chemical, and physicochemical characteristics of

clathrochelate complexes as well as relationships between them have been examined.

Special interest has focused on the redox and photochemical properties of sarcophaginates and sepulchrates, since they offer ample possibilities for the use of such compounds as sensitizers and electron carriers in photocatalytic solar energy conversion processes and in solving a variety of other practical problems. The invaluable contributions made by A. M. Sargeson and his group to the development of this trend together with some aspects of the synthesis and structure of these types of clathrochelates (see reviews [3-6]) should particularly be stressed. Undoubtedly interesting is the specific selectivity of macrobicyclic tris-dioximate formation reactions, enabling one to perform directed synthesis of analytical reagents exhibiting high selectivity together with high sensitivity.

Although clathrochelates are most closely related to thio- and aza-macrocyclic *d*-metal complexes, they display several specific features of their own. The number of publications is also essentially different. Numerous papers and several monographs dealing with classical macrocyclic complexes have been published [7-17], whereas the quantity of papers concerning the chemistry and physical chemistry of clathrochelates does not exceed three hundred.

For further research in this promising field of chemistry, the experimental and theoretical data on clathrochelates should be generalized and analysed. This is the aim of this monograph. Chapter 1 gives general concepts of complexes with encapsulated metal ions, discusses basic specific features of these compounds, considers and characterizes the main types of compounds with encapsulated metal ions and the main classes of clathrochelates, and includes the current nomenclature. Chapter 2 deals with the pathways of clathrochelate synthesis and the general procedures for the synthesis of macrobicyclic tris-dioximates, phosphorus-containing tris-diiminates, sepulchrates, sarcophaginates, and polyene and other types of clathrochelate complexes. Chapter 3 concerns studies of the electronic and spatial structure of clathrochelate complexes. In Chapter 4, the kinetics and mechanism of synthesis and decomposition reactions of macrobicyclic tris-dioximates, sarcophaginates, and sepulchrates in solution and gas phases are discussed. Chapter 5 considers the electrochemical, photochemical, and some other characteristics of



clathrochelates and their applications associated with these characteristics.

Finally, the practical applications of the unique properties of clathrochelates and perspectives on the synthesis of new clathrochelates are described in Chapters 6 and 7, respectively.

We wish to thank Ms. Elena Kiba and Mr. Slava Levitsky, who inestimably helped with the manuscript, and Ms. Gretchen Becker (Vermont, USA) for linguistic editing. We are much indebted to Prof. Alexander Nazarenko (SUNY, Buffalo) for many years of fruitful collaboration. We rather regret that he could not take part in the present project. We also thank Dr. Igor Fritsky and Dr. Oleg Varsatskii for their competent discussion about this book and fruitful ideas.

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*April 2002*

# A LIST OF MAIN ABBREVIATIONS

| | | | |
|---|---|---|---|
| ac | – acetate ion | L | – ligand |
| acac | – acetylacetone | LFSE | – ligand-field stabilization energy |
| Am | – amine | | |
| AN | – acetonitrile | LUMO | – lowest unoccupied molecular orbital |
| AO | – atomic orbital(s) | | |
| bpy | – 2,2'-bipyridine | M | – metal ion |
| bpz | – 2,2'-bipyrazol | m | – multiplet |
| Bs | – benzene sulphonate radical | mal | – malonate ion |
| | | Me | – methyl radical |
| Bu | – *n*-butyl radical | MeIz | – N-methylimidazole |
| CD | – circular dichroism | MO | – molecular orbital(s) |
| cp | – cyclopentadien | $mv^{2+}$ | – methylviologen (dication) |
| CTB | – charge transfer band | NHE | – normal hydrogen electrode |
| d | – doublet | | |
| DCD | – differential circular dichroism | phen | – 1,10-phenanthroline |
| | | 1,2pn | – 1,2-diaminopropane |
| DEA | – diethylamine | 1,3pn | – 1,3-diaminopropane |
| DMF | – dimethylformamide | Py | – pyridine |
| DMSO | – dimethylsulphoxide | q | – quartet |
| EDTA | – ethylenediamine-tetraacetate ion | QS | – quadrupole splitting in Mössbauer spectra |
| EFG | – electric field gradient | $r_i$ | – physical (Shannon) ionic radius |
| en | – ethylenediamine | s | – singlet |
| Fc | – ferrocenyl radical | SCE | – standard calomel electrode |
| Hal | – halogenide substituent | sh | – shoulder |
| HOMO | – highest occupied molecular orbital | t | – triplet |
| | | TAP | – trigonal antiprism |
| HSAB | – hard and soft acids and bases (theory) | tart | – tartrate ion |
| | | THF | – tetrahydrofuran |
| IEC | – ion-exchange chromatography | TOF | – triethyl orthoformate |
| | | TP | – trigonal prism |
| IS | – isomeric shift in Mössbauer spectra | tren | – tris(2-aminoethylamine) |
| | | Ts | – tosyl radical |
| Iz | – imidazol | | |

# Table of contents

*Chapter 1*

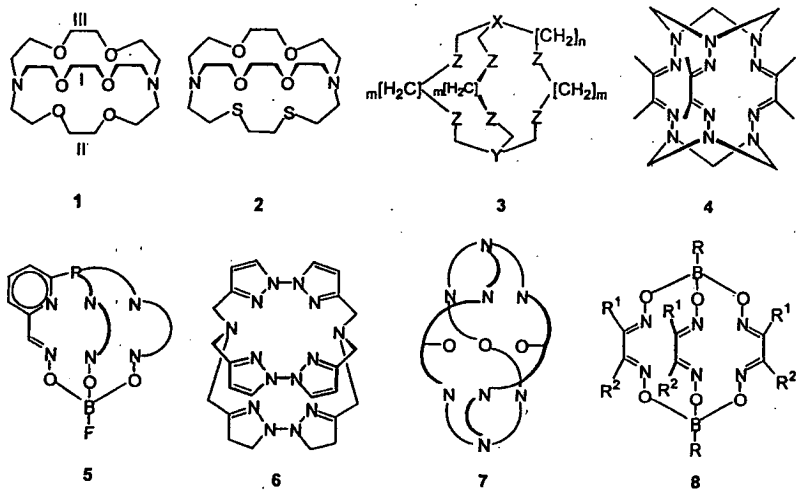
# Fundamental concepts of complexes with encapsulated metal ions

Because the definition of metal ion encapsulation or its absence is, to a certain extent, ambiguous, we first describe the conventional criteria that we use to restrict the scope of the compounds to be considered. The major signs of complexation (formation of a complex) with an encapsulated metal ion are (a) a three-dimensional cavity (capsule, cage) produced by a macropolycyclic ligand and (b) metal ion coordinating heteroatoms in this cavity that isolate this metal ion from the environment.

The ligand capable of forming a cage must comprise at least two macrocyclic fragments (Scheme 1).

As we define them, the key difference between macrobicyclic ligands and bis-macrocyclic ones is that in the former, each of the fragments (I, II, III) is involved in the formation of two macrocycles (in contrast to bis-macrocycles) containing fourteen or more atoms in the cycle and four donor atoms, which is consistent with Melson's definition [9] of macrocycles (the number of atoms in the cycle is nine or more, and the number of donor atoms is three or more). Most encapsulating ligands contain two atoms that belong to all fragments of a macrobicyclic ligand, called ***capping*** atoms (e.g., the tertiary nitrogen atoms in **1**, **2**, **6**, **7**; boron, tin, germanium, etc. atoms in **8**; carbon or nitrogen atoms in **3**; phosphorous and boron atoms in **5**, Scheme 1). In ligand **4**, 1,3,5-triazacyclohexane ring acts as a capping group.

A metal ion encapsulated in the three-dimensional ligand cavity must be an acceptor bonded to the donor groups of all macrocycles forming the cage framework. This is time either when the metal ion size corresponds to the ligand cavity size or when the cavity can be transformed under the influence of the metal ion so that the distance between the central ion and the donor atoms of the cage is not over the sum of their ionic or covalent radii. In addition to the geometric parameters, the thermodynamic and kinetic stability of




Scheme 1

clathrochelate complexes is determined by the electronic structure of the encapsulated metal ion and the nature of the ligand.

## 1.1. CLASSIFICATION OF MACROPOLYCYCLIC LIGANDS

The nature of the donor atoms is one of the most important characteristics of macrocyclic ligands [11] and has been employed as a criterion for a classification of macrocyclic compounds. The classification of the macropolycyclic encapsulating ligands is based on the nature of the donor atoms and the type of donor groups that appear to be the best.

I. Polyazamacropolycycles. Nitrogen atoms act as donor atoms.

I.I. Macropolycyclic polyamines. Amine and/or hydroxylamine fragments act as donor groups.

I.II. Macropolycyclic tris-dioximes. Oxime groups act as donor groups.

I.III. Macropolycyclic phosphorous-containing tris-diimines. Oxime and heterocyclic nitrogen-containing fragments act as donor groups.



I.IV. Macropolycyclic polyene tris-diimines. Azomethine fragments act as donor groups.

I.V. Macropolycyclic polyaromatic tris-diimines. Heterocyclic nitrogen-containing fragments act as donor groups.

II. Polyazathiomacropolycycles. Nitrogen and sulphur atoms act as donor atoms.

III. Polyazaselenomacropolycycles. Nitrogen and selenium atoms act as donor atoms.

IV. Polythiomacropolycycles. Sulphur atoms act as donor atoms.

V. Polyoxothiomacropolycycles. Sulphur and oxygen atoms act as donor atoms.

VI. Polyazaoxothiomacropolycycles. Nitrogen, sulphur and oxygen atoms act as donor atoms.

VII. Polyazaoxomacropolycycles. Nitrogen and oxygen atoms act as donor atoms.

VIII. Polyoxomacropolycycles. Oxygen atoms act as donor atoms.

VIII.I. Macropolycyclic polyethers. Ether fragments act as donor groups.

VIII.II. Macropolycyclic tris-diols. Hydroxyl groups act as donor groups.

It is evident that this classification is incomplete, and as new data become available, more groups and subgroups of encapsulating ligands will be included.

The ligands of the first two groups form stable complexes mainly with transition metal ions. The properties of ligands belonging to these groups are close to those of synthetic polyazamacrocyclic ligands. The ligands are usually referred to as ***clathrochelants*** and their complexes as ***clathrochelates***. However, the terms "*polyazacryptands*" and "*polyazacryptates*" also occur. Metal ions with closed electronic shells are effectively encapsulated by the ligands of groups VI and VII. The ligands of groups IV-VIII (except subgroup VIII.II) are usually called ***cryptands*** and their complexes ***cryptates***. Cryptates have properties similar to those an oxocrown ethers. ***Catenandes*** are the ligands of subgroup VIII.II.

In comparison with their role in macrocyclic complexes, the role of steric factors and the correspondence of the cavity size to the metal ion size drastically increase in macrobicyclic compounds with an encapsulated metal ion. The degree of freedom in macrocyclic complexes related to the location of the metal ion outside the plane of

ligand donor atoms partly disappears in macrobicyclic complexes. The increase in the role of steric factors from monodentate to encapsulating ligands may be represented as follows [18, 19]:

| Type of ligand | Degrees of freedom |
|---|---|
| Monodentate ligand | 3 |
| Bidentate, chelating ligand | 2 |
| Polydentate, macrocyclic ligand | 1 |
| Encapsulating, macropolycyclic ligand | 0 |

In fact, steric restrictions are not rigorous, and a substantial degree of freedom can be retained due to the flexibility of the encapsulating ligand and its capacity to undergo conformational changes.

In this book, we discuss only complexes with group I and II ligands, containing nitrogen atoms or nitrogen and sulphur atoms as donor atoms, for which we adopt the name "***clathrochelates***". This term was introduced by Daryl H. Busch [1] for cage chelate complexes, and is not a direct derivative from "***clathrate***". Both these terms just have a common root from the Latin ***cläthrätus***, to furnish with lattice (*Webster's Encyclopedic Unabridged Dictionary of the English Language*, Portland House, New York, 1989, P. 273).

## 1.2 NOMENCLATURE, ABBREVIATIONS AND CLASSIFICATION OF CLATHROCHELATES

Each of the known clathrochelates may be named according to the IUPAC regulations, but an extreme awkwardness of such name causes considerable difficulties in usage. For instance, in accordance with the IUPAC nomenclature, the clathrochelate ligand 3 (Scheme 1), when $n = m = 2$, should be called

1,3,6,8,10,13,16,19-octaazabicyclo-(6,6,6)-eicosane,

and the ligand 8, where R = BOH and $R^1,R^2 = (CH_2)_5$, as

1,13-bis(oxybora)-2,12,14, 24,25,25-hexaoxa-3,11,15,23,26,34-hexaazapentacyclo-[11.11.11.$0^{4'10}0^{16'22}0^{27'33}$]pentatriaconta-3,10,15,22,26,33-hexaene.

The nomenclature proposed by Melson and Busch [9, 20] for monomacrocyclic compounds is not applicable to clathrochelates since



Table 1.
Symbols of the apical substituents in the capping fragments of sarcophaginates and sepulchrates.

| Prefix | Group | Prefix | Group |
|---|---|---|---|
| aza | –N= | CA | –COOH |
| AMH | $-N^+H_3$ | CAA | $-COO^-$ |
| $NH_2OH$ | $-N^+H_2OH$ | AM | $-NH_2$ |
| MeAMH | $-N^+H_2CH_3$ | NHOH | –NHOH |
| $Me_2AMH$ | $-N^+H(CH_3)_2$ | MeAM | $-NHCH_3$ |
| $Me_3AMH$ | $-N^+(CH_3)_3$ | $Me_2AM$ | $-N(CH_3)_2$ |
| NO | $-NO_2$ | EF | $-COOC_2H_5$ |
| ME | $-CH_3$ | Nl | –NO |
| HO | –OH | HM | $-CH_2OH$ |
| AA | $-NHCOCH_3$ | CN | –CN |
| TsAM | –NHTs | PI | –NPhth[a] |
| SalAMH | $-N^+H_2CH_2$-2-$C_6H_5OH$ | TerIM | $-NCH$-4$C_6H_5CHO$ |
| BzAMH | $-N^+H_2CH_2C_6H_5$ | SalAM | $-NHCH_2$-2-$C_6H_5OH$ |
| TerAMH | $-N^+H_2CH_2$-4-$C_6H_5OH$ | BzAM | $-NHCH_2C_6H_5$ |
| BzIM | $-NCHC_6H_5$ | TerAM | $-NHCH_2$-4-$C_6H_5OH$ |
| CL | –Cl | ClME | $-CH_2Cl$ |

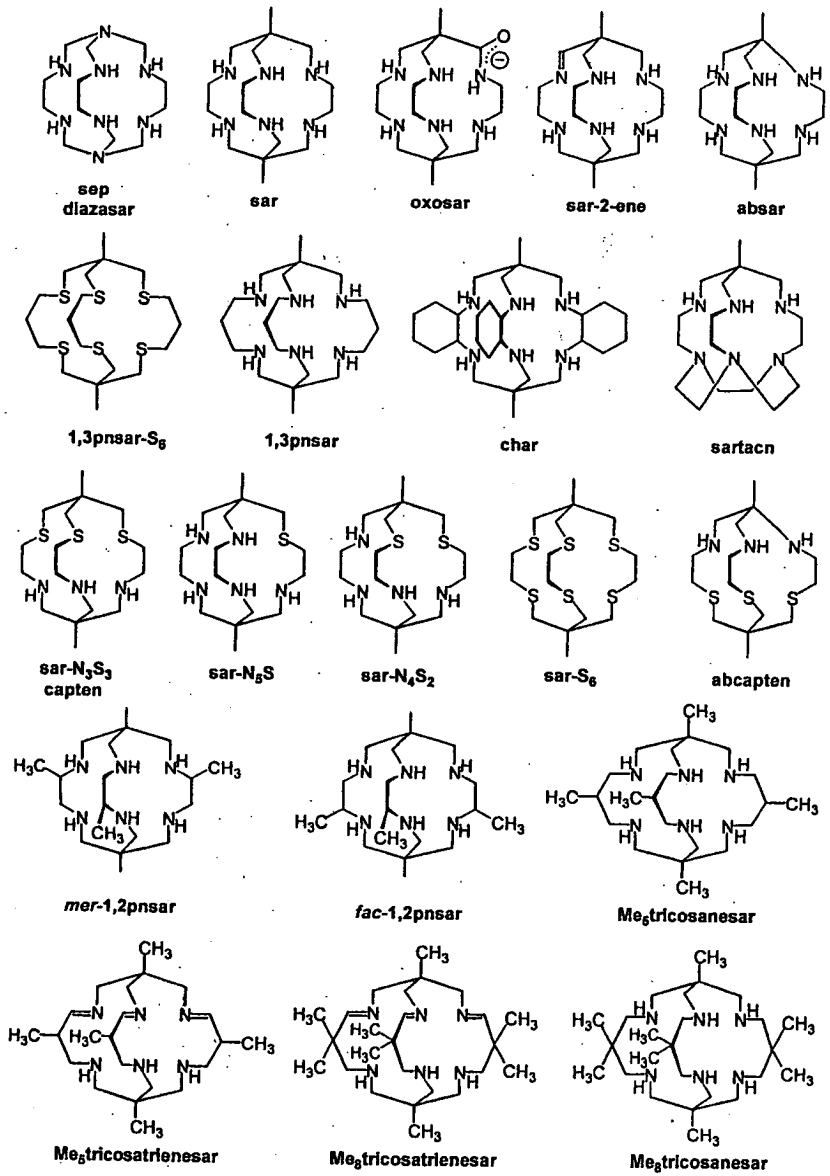
[a] NPhth is phthalimide

in this nomenclature the macroring is chosen as a basis, and the name incorporates abbreviations for the substituents. Each group of clathrochelates has its own system of names and symbols. The abbreviations for ligands of subgroup I.I. complexes include the symbol for the encapsulating framework with an indication of the substituents on this cage. The framework with the diamine chelate fragments and carbon atoms in the apical positions is called ***sarcophagine*** (*sar*), and those with nitrogen atoms in the apical positions, ***sepulchrate*** (*sep*) or (*diazasar*). If the clathrochelate framework is changed, its symbol is accordingly changed either by adding case letters or by giving another name to the framework (Scheme 2).

The ligand *capten* belongs to ligands of group II, but its properties are close to those of subgroup I.I.

The substituents at the carbon atoms in the apical positions and at the coordinated nitrogen atoms are denoted by placing the appropriate prefixes to framework symbol (Table 1).

Complexes with type I.II ligands are usually referred to as boron (tin, germanium, silicon, antimony)-capped macrobicyclic dioximates (oximehydrazonates, azineoximates). Their abbreviated




Scheme 2



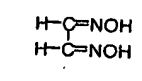
name includes the conventional symbol for dioximate (or oximehydrazonate, or azineoximate) fragments and the capping groups, e.g. $MNx_3(BF)_2$, where $Nx^{2-}$ is cyclohexanedione-1,2-dioxime (nioxime) dianion. The initial dioximes, oximehydrazones, and azineoximes used for the synthesis of clathrochelate complexes have the symbols given in Scheme 3.

Macrobicyclic iron(II) complexes of this type have been obtained for the aliphatic acyclic and alicyclic, aromatic dioximes as well as halogenide and functionalized ones by cross-linking with boron-containing agents of different nature (hydrogen; halogens; alkyl, aryl, hydroxyl, alkoxyl or functionalizing groups as the substituents at the boron atom) or tin-, germanium-, and antimony-containing ones (halogenide, oxygenide, perfluoroorganyl, and organyl substituents). The capping with other Lewis acids has scarcely been examined. Nevertheless, there are data available that macrobicyclic complexes may be prepared *via* a template cross-linking with compounds of most other *p*-block elements [21], in particular, bismuth, arsenic, etc.

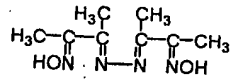
The formation of such boron-capped compounds is less characteristic of cobalt (III); more characteristic is the formation of trihalogenotin-capped clathrochelates. Syntheses of the boron-capped cobalt(III) $CoD_3(BR)_2$ complexes have been performed under relatively rigid conditions for certain dioximes ($H_2Dm$, $H_2Nx$, $H_2Bd$) and with most effective capping agents (R = F, $C_6H_5$, $n$-$C_4H_9$). In this case, clathrochelate complexes are positively charged and have been isolated as salts with bulky inorganic anions. The cobalt(II) complexes have been obtained *via* reduction of cobalt(III) compounds. The trihalogenotin-capped clathrochelate cobalt(III) dianions have been isolated as salts with bulky organic cations.

Several macrobicyclic ruthenium, nickel, zinc, manganese, copper, chromium, magnesium, and lithium complexes, as well as two free macrobicyclic tris-dioximate ligands, have also been synthesized.

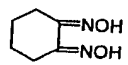
Clathrochelates derived from phosphorus-containing tris-diimine ligands (subgroup I.III) have been prepared for nickel, cobalt, zinc, and iron ions. These complexes are capped by the phosphorus atom bonded to the pyridine ring and by the boron atom *via* oxygen bridges. Nickel, copper, cobalt, and zinc semiclathrochelates have also been isolated. These complexes are capped by the phosphorus atom, and the three oxygen atoms of the second fragment are hydrogen-bonded by two protons.



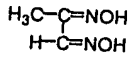

glyoxime
($H_2Gm$)



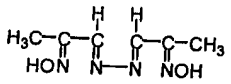

diacetylazineoxime
($H_2DAO$)



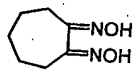

nioxime
($H_2Nx$)



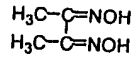

methylglyoxime
($H_2Mm$)



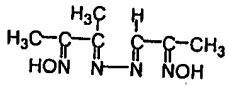

methylglyoxalazineoxime
($H_2IAO$)



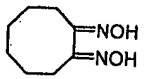

heptoxime
($H_2Gx$)



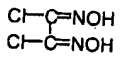

dimethylglyoxime
($H_2Dm$)




diacetylmethylglyoxalazineoxime
($H_2TMAO$)




octoxime
($H_2Ox$)

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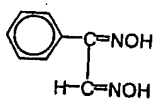
($H_2Cl2Gm$)




phenylglyoxime
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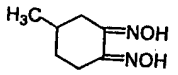
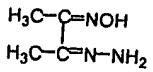
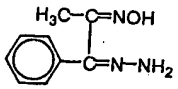


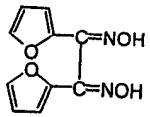

4-methylnioxime
($H_24MNx$)



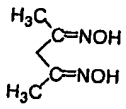

diacetylmonooxime
hydrazone
(HDXO)



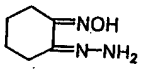

benzylacetylmonooxime
hydrazone
(HPXO)



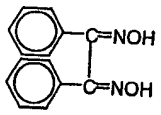

α-furyldioxime
($H_2Fd$)




acetylacetonedioxime
($H_2Ad$)




cydohexanedione-1,2-monooxime
hydrazone
(HCXO)




α-benzyldioxime
($H_2Bd$)

**Scheme 3**



Compounds of the sarcophaginate and sepulchrate type capped by the carbon or nitrogen atom *via* methylene units have been most thoroughly studied. Complexes of numerous metals (Co, Cr, Mn, Ag, Fe, Ni, Cu, Rh, Pt, Ru, Hg, V, In, Ga, Cd, Mg) ions with various apical substituents have been synthesized with cage ligands, whose ethylenediamine fragments act as chelating groups. A predominant majority of complexes was formed with an encapsulated cobalt ion. In these complexes, capping groups are either the same or different: N and C-R, where R is a substituent listed in Table 1. Cobalt(III) complexes with 1,2- and 1,3-propanediamine, and cyclohexanediamine chelate cycles have also been prepared.

Three classes of clathrochelates, as well as clathrochelates not included in these classes and discussed in a separate section, have the following common properties in addition to those previously mentioned:

- the geometry of all hexadentate clathrochelates is intermediate between a TP and a TAP;
- in the majority of cases, the clathrochelate ligand template forms on the metal ion matrix; the number of templates for given ligand is limited;
- the first rate-determining stage of the synthesis of clathrochelates is the formation of the corresponding semiclathrochelate;
- all clathrochelates are very stable and inert to metal ion and ligand substitution.

There are also differences that characterize each class of clathrochelates:

a) the clathrochelate ligands of types 5 and 8 (Scheme 1) in most cases exist only in complexes with metal ions and cannot be isolated in a free form. In the majority of cases, type 3 clathrochelate ligands have been obtained by demetallation of the corresponding cobalt complexes and used for the synthesis of the compounds with metal ions incapable of serving as template agents. The preliminarily synthesized macrobicyclic tris-phenantroline, tris-bipyridine, and sarcophagine-$S_6$ clathrochelate ligands have also been used for the synthesis of corresponding clathrochelates;

b) the formation of type 8 compounds is specially selective, and type 3 ligands are the most universal;

c) in type 8 compounds, a certain oxidation state, e.g. $Fe^{2+}$ or $Co^{3+}$, is stabilized; the formation of stable compounds in two oxidation states is characteristic of type 3 compounds;
d) type 3 complexes, unlike most complexes of other types, are reactive. They undergo redox and substitution reactions involving neither capsule destruction nor a change in the central ion state, which makes it possible to synthesize a number of clathrochelate complexes of this type with different substituents in the chelating and capping fragments.



*Chapter 2*

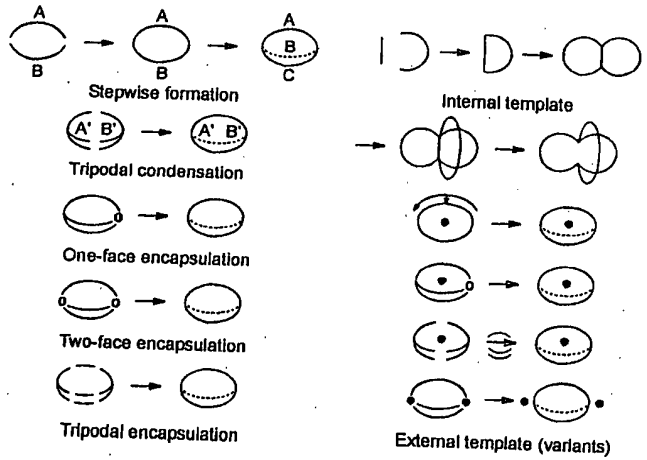
# Synthesis of clathrochelates

The striking results achieved in the chemistry of cryptands, synthetic ionophores, and ionic and molecular receptors are governed to a great extent by successes in developing synthetic routes that allow one the desired variations in the structure and properties of such compounds by introducing functional groups and modifying the molecule framework. Therefore, the development of methods for the synthesis of clathrochelates with the targeted geometry, symmetry, and functionality has become an extremely urgent task.

Clathrochelates may be isolated using conventional methods for the preparation of macrocyclic compounds described elsewhere in detail [7-17]. However, certain specific features observed in both the formation and the structure of these complexes drastically increase the role of template synthesis in their preparation. This is largely because some clathrochelate ligands, such as macrobicyclic tris-dioximates and phosphorus-containing tris-diiminates, in most cases are not available in the free state and can arise only from a template reaction on the metal ion. Some peculiarities of their formation are attributed to the conjugated $\pi$-bonds in $\alpha$-dioxime and $\alpha$-diimine fragments essentially enhancing the structural rigidity, as well as the rigidity of a capping (cross-linking) fragment that may be relatively easily detached with subsequent destruction of the macrobicyclic framework.

Metal ion directed (template) syntheses of the macrobicyclic complexes are effected through cyclization of the preformed tris-complexes or semiclathrochelate as well as *via* interaction of metal ion bis-complexes with cross-linking agents.

In some cases, a free clathrochelate ligand has been isolated after its template construction on the metal ion and demetallation of the resultant complexes. In particular, this has made it possible to synthesize sarcophaginates of many metals incapable of forming clathrochelates *via* direct template synthesis; they are formed from




**Scheme 4**

the appropriate free ligands preliminarily obtained by demetallation of cobalt(III) complexes.

A number of clathrochelate ligands (Sections 2.3 and 2.4) can be preliminarily synthesized by conventional organic chemistry procedures. However, the role of the template effect can not be discounted either. In the majority of cases, alkali metal ions (most common $Na^+$ and $Cs^+$ ions) presumably act as templates that are then readily extruded from the clathrochelate ligand cavity.

The general strategy for the synthesis of macrobicyclic compounds may be represented by Scheme 4 proposed by Lehn and coworkers [22].

The clathrochelates may arise from an exchange reaction between initial complexes with labile capping fragments and an excess of a more efficient cross-linking agent (Scheme 5).

For instance, this reaction pathway has been employed for the preparation of tin-capped iron(II) tris-dioximates by the treatment of hydroxy- and alkoxyboron-capped clathrochelate complexes with


**Scheme 5**



excess tin tetrachloride, and, *vice versa*, fluoroboron-capped complexes have been formed by the interaction of the initial tin-capped iron(II) dioximates with an excess of boron trifluoride etherate.

The isolated free ligands may be modified and further employed for the synthesis of novel clathrochelate complexes. The latter also arise from modification reactions of complexes with reactive ligand groups (precursors). Such reactions are essential for synthesis of the sepulchrates, sarcophaginates, and apical- and ribbed-functionalized tris-dioximates. In these cases, the reactivity of peripheral ligand groups, substituents in ribbed fragments, and coordinated amino groups have been used. The redox processes involving the central metal ion and a macrobicyclic ligand also belong to the complex modification reactions.

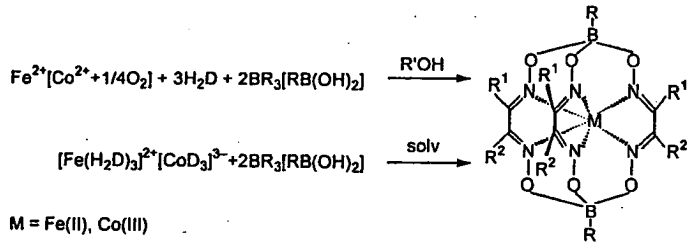
## 2.1 SYNTHESIS OF MACROBICYCLIC TRIS-DIOXIMATES

In the majority of cases, the formation of macrobicyclic metal tris-dioximates is stipulated by the interaction of the reactive oxime groups in tris-dioximate complexes with Lewis acids. The most efficient capping agents have proved to be trigonal organic and inorganic boron compounds.

Christopherson and Sandell [23] suggested that the abnormally high solubility of nickel(II) $Ni(HDm)_2$ dimethylglyoximate in borate buffer is caused by substitution of the hydrogen bond protons of the dioximate fragments by boron atoms to give weak complexes. Schrauzer [24], Umland and coworkers [25, 26] have reported that the macrocyclization of nickel dimethylglyoximate yields $Ni(DmBR_2)_2$ complexes (where R is F, $C_6H_5$, $n$-$C_4H_9$, or $CH_3$). Thus, dioximate fragments in square-planar bis-dioximates have been demonstrated to be subjected to cross-linking, forming macrocyclic complexes. This route has been used by many workers engaged in the synthesis of macrocyclic *d*-metal bis-dioximates [27-37]. Moreover, the fact that the tris-dioximate complexes can be capped with boron-containing agents facilitates the synthesis of macrobicyclic compounds with an encapsulated metal ion.

Cobalt complexes of this type were initially isolated by Boston and Rose [2] and independently by Umland and coworkers [38]. Boron-capped iron(II) and cobalt(III) tris-dioximates have been obtained by two main routes: a direct template reaction on the metal ion and the

cross-linking of the initial nonmacrocyclic tris-dioximates (Reaction 1).

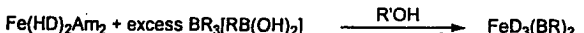



(1)

The first route proved to be the most universal one. Owing to a shift in the equilibrium brought about by the formation of a clathrochelate complex, it permits one to prepare a number of compounds in relatively high summary yields. The second pathway, which is carried out in aprotic media, offers higher yields than the first one. However, a low yield of the nonmacrocyclic tris-complex at the first stage imposes restrictions on the scope of this method.

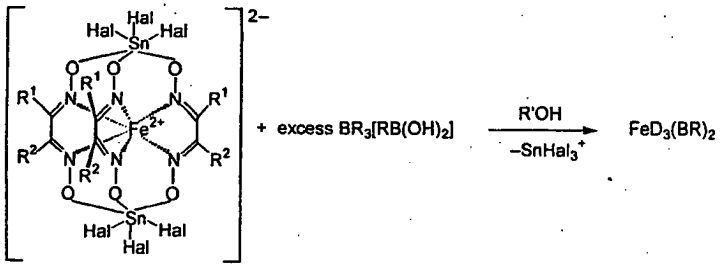
The yields of desired products have been improved by the azeotropic distillation of water from the reaction mixture and the resultant $H^+$ ion neutralization.

The synthesis of boron-capped iron(II) tris-dioximates has also been implemented using two other methods: the rearrangement of the Tchugaev type $Fe(HD)_2Am_2$ bis-dioximates in the presence of boron-containing Lewis acids:




(2)

and by a capping group exchange (re-metallation) reaction:



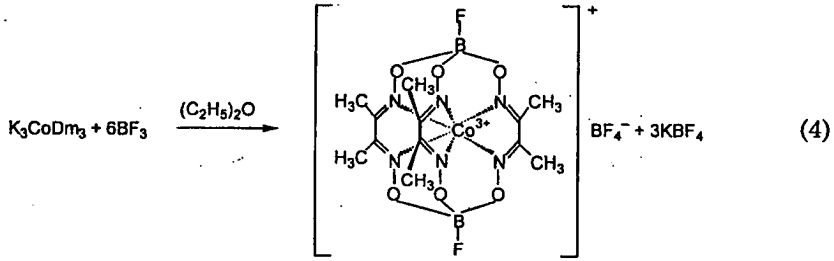

(3)

Reactions 2 and 3 take place only in the presence of strong Lewis acids, e.g., $BF_3$, which is the most efficient agent among boron-containing Lewis acids. The fact that alkyl- and arylboron-capped compounds have easily been produced *via* Reaction 1 is due to a relatively high energy of their crystal lattice (as a result compounds precipitate) as well as to decrease in the decomposition reaction rate, which leads to an equilibrium shift in the direction of their formation.



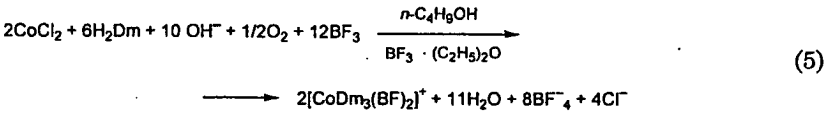
The proposed schemes for the synthesis of macrobicyclic tris-dioximates have most readily been realized in high yields for alicyclic dioximes, having a *cis*-conformation both in crystals and in solutions. The change of the acyclic dioxime conformation from *trans* to *cis* during complexation decreases the stability of the compounds formed.

For the first time, a preformed nonmacrocyclic cobalt(III) tris-dimethylglyoximate was cross-linked with boron trifluoride in diethyl ether [2]:




(4)

The preparation of the $[CoDm_3(BF)_2](BF_4)$ complex was described in detail [39]. Its disadvantage is a low (13%) yield of an intermediate $K_3CoDm_3$ product. A more facile and efficient Reaction 5 requires no isolation of an intermediate nonmacrocyclic tris-dioximate [40]:



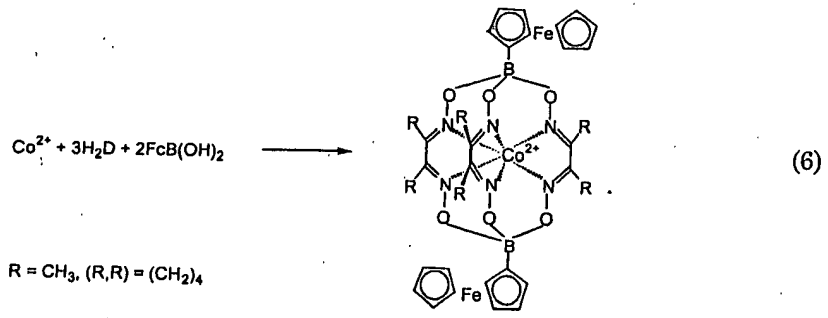

(5)

The $BF_4^-$ anion in the clathrochelate $[CoDm_3(BF)_2](BF_4)$ complex can readily be replaced by another large inorganic anion (e.g. $PF_6^-$) *via* an exchange reaction occurring in aqueous-acetonitrile solution in the presence of a great excess of the substituting anion salt [39]. The reduction of the $[CoDm_3(BF)_2](BF_4)$ clathrochelate with NaI solution in acetone yielded a macrobicyclic cobalt(II) $CoDm_3(BF)_2$ complex. The synthesis of the latter *via* a template condensation on the $Co^{2+}$ ion was not yet successful.

A template condensation on the $Co^{3+}$ ion proved to be the most efficient approach to the preparation of such cobalt compounds. A similar route was employed for the synthesis of a macrobicyclic cobalt(III) $[CoNx_3(BF)_2](BF_4)$ and $[CoBd_3(BF)_2](BF_4)$, $[CoBd_3(BC_6H_5)_2](BF_4)$ nioximates and α-benzyldioximates, when boron trifluoride and phenylboronic acid were used as cross-linking agents [41, 42]. The $[CoNx_3(BF)_2](BF_4)$ complex was also synthesized *via* capping of the nonmacrocyclic $K_3CoNx_3$ complex with boron fluoride [41]. This procedure was used to prepare $[CoDm_3(BC_6H_5)_2](BF_4)$, $[CoNx_3(BC_6H_5)_2](BF_4)$, $[CoDm_3(Bn\text{-}C_4H_9)_2](BF_4)$, and $[CoNx_3(Bn\text{-}C_4H_9)_2](BF_4)$ clathrochelates by cross-linking of the analogous tris-complexes with a reactive boron-containing agent ($C_6H_5BCl_2$ or $n\text{-}C_4H_9BCl_2$) in methylene chloride, accompanied by replacement of the $Cl^-$ anion by the $BF_4^-$ anion on an ion-exchange column.

The reduction of cobalt(III) complexes with NaI solution in acetone yielded analogous macrobicyclic cobalt(II) $CoBd_3(BF)_2$ and $CoNx_3(BF)_2$ complexes [42]. The formation of these complexes, as well as $CoDm_3(BC_6H_5)_2$, $CoDm_3(Bn\text{-}C_4H_9)_2$, $CoNx_3(BC_6H_5)_2$, $CoNx_3(Bn\text{-}C_4H_9)_2$, and $CoBd_3(BC_6H_5)_2$ clathrochelates in acetonitrile solution *via* reduction of the corresponding cobalt(III) clathrochelates with ferrocene was studied in research reported in Ref. 41, but their isolation as solids was not described.

In the synthesis of the boron-capped cobalt(II) tris-dioximates, ferrocenylboronic acid was also used as a capping agent [43]. Reaction of this Lewis acid with anhydrous $CoCl_2$ and dioximes in oxygen-free methanol gave clathrochelate $CoNx_3(BFc)_2$ and $CoDm_3(BFc)_2$ complexes:




(6)

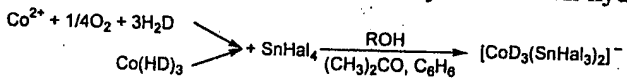


Cobalt(III) tris-dioximates were also cross-linked with other Lewis acids, such as $SnCl_4$ and $SiCl_4$ [39]. Reaction of $K_3CoDm_3$ in methylene chloride with anhydrous $SnCl_4$ resulted in the macrobicyclic $[CoDm_3(SnCl_3)_2]^-$ anion, which was isolated as an ionic associate with a bulky $(n\text{-}C_3H_7)_4N^+$ cation [39].

Attempts to use tin(IV) tetraalkylates and trialkylhalogenides as capping agents met with failure just like those undertaken with cobalt(III) tris-dioximates and tin tetrafluoride as a capping agent. The latter appears to be explained by the difficulties encountered in the detachment of the fluoride ion bonded to the tin atom and the formation of by-products (cobalt(III) and tin(IV) bis-dioximates). It is evident that in this case steric factors are negligible because the fluorine substituent is small [44].

For tin(IV) bromide, the halogenide ion detachment apparently takes place much more readily compared with that of $SnF_4$. However, the bulky bromine atom causes steric hindrances due to its interaction with the substituents at the α-dioxime fragments. In particular, attempts to obtain clathrochelate tribromotin-capped cobalt(III) α-benzyldioximate and α-furyldioximate were not successful, whereas the corresponding trichlorotin-capped complexes were obtained [45].

Tin-capped clathrochelate cobalt(III) tris-dioximates were synthesized by a procedure similar to Reaction 1 in the presence of organic bases (amines or tetra-*n*-butylammonium hydroxide):




(7)

Hal = Cl, Br
$H_2D$ = $H_2Gm$, $H_2Mm$, $H_2Dm$, $H_2Bd$, $H_2Nx$

A number of compounds of this type were obtained and isolated as complex acids or salts with organic cations when tin(IV) tetrachloride and tetrabromide were used as the capping agents [44, 45].

Certain α-dioximate $H[CoD_3(SnHal_3)_2]$ complex acids were isolated at the first stage without the addition of amine or with its addition in small amounts. The subsequent addition of amines resulted in the formation of the corresponding ionic associates.

A similar reaction of $K_3CoDm_3$ with $SiCl_4$ in boiling THF enabled one to prepare a macrobicyclic $[CoDm_3(SiO)_2]\cdot HPF_6$ complex [39]:

$$K_3CoDm_3 + 2SiCl_4 \xrightarrow[t^\circ]{THF} [CoDm_3(SiCl_2)_2] \xrightarrow[CH_3OH + H_2O]{NaPF_6;\ H^+} [CoDm_3(SiO)_2] \cdot HPF_6 \quad (8)$$

This compound was isolated as a polymeric gel. Macrobicyclic fragments in the polymer chain are linked by Si–O–Si bridging fragments. It was claimed [39] that this clathrochelate may be either a low-spin cobalt(II) compound or a mixture of cobalt(II) and cobalt(III) compounds. However, taking into account the polymeric nature of the complex and the difficulties encountered in its isolation and investigation, one may conclude that the data reported [39] are not sufficient for its unambiguous identification.

Transition metal aqua ions and their complexes with amines have also been utilized as capping agents in the synthesis of macrobicyclic cobalt tris-dioximates [46]. The reactions of nonmacrocyclic $K_3CoDm_3$ tris-dimethylglyoximate with $dienCrCl_3$, $dienCoCl_3$, and $tameCo(NO_3)_3$ complexes (where *dien* is diethylenetriamine and *tame* is 1,1,1-tris(aminomethyl)ethane) and $Li_3CoDm_3$ with $[Zn(H_2O)_6]^{2+}$ and $[Ni(H_2O)_6]^{2+}$ aqua ions resulted in the formation of the corresponding clathrochelate $[CoDm_3(dienCr)_2](PF_6)_3 \cdot C_2H_5OH$, $[CoDm_3(dienCo)_2](PF_6)_3 \cdot CH_3OH$, $[CoDm_3(Ni(H_2O)_3)_2](PF_6) \cdot 4H_2O$, and $[CoDm_3(Zn(H_2O)_3)_2](PF_6) \cdot 3H_2O$ complexes. The interaction between the two last compounds and free *dien* ligand permitted one to obtain the $[CoDm_3(dienNi)_2)](PF_6) \cdot 4H_2O$ and $[CoDm_3(dienZn)_2)](PF_6) \cdot 2H_2O$ clathrochelates [46].

Synthesis of macrobicyclic $MDm_3(BR)_2$ complexes (where M is nickel (paramagnetic), iron and cobalt ions; R is $C_6H_5$ and $n$-$C_4H_9$) was reported by Umland and coworkers [38]. However, the formation of nickel complexes of this type was not further confirmed.

A series of boron-capped iron(II) tris-dimethylglyoximates was obtained in high yield by direct template reactions [47, 48]. Iron ions serve an "organizational role" by providing a template on which three dimethylglyoxime fragments become bound *prioro* to the reaction with boron-containing agents either in alcohol or water (Reactions 9 and 10).

$$Fe^{2+} + 3H_2Dm + 5OH^- \xrightarrow[n\text{-}C_4H_9OH]{BF_3 \cdot (C_2H_5)_2O} FeDm_3(BF)_2 + H^+ + 4BF_4^- \quad (9)$$

$$Fe^{2+} + 3H_2Dm + 2H_3BO_3 \xrightarrow{ROH} FeDm_3(BOR)_2 + 2H^+ + 6H_2O \quad (10)$$

R = H, $CH_3$, $C_2H_5$, *iso*-$C_3H_7$, $n$-$C_4H_9$

It was noted that the base must be slowly added to the iron(II) salt, dimethylglyoxime, and boron trifluoride etherate solution in *n*-butanol. The reaction mixture must be slightly acidic; otherwise, the by-products formed contaminate the resultant complex and reduce its yield. If no base is added, the product is formed over a period of days [47]. The process was accelerated by reaction mixture refluxing for several minutes [49, 50]. The fluoroboron-capped complexes, prepared in the absence of the base, have the advantage that they are free of by-products.



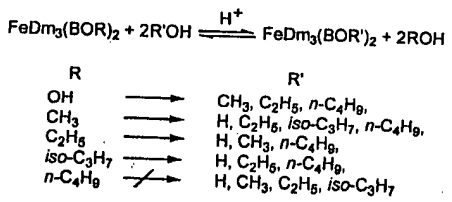
An iron(II) salt can be replaced by an iron(III) salt or metallic iron in the synthesis of the $FeDm_3(BF)_2$ and $FeDm_3(BOR)_2$ complexes. The reduction of iron(III) ions to iron(II) ions takes place in the first case and gaseous hydrogen is released in the second case. Attempts to prepare a clathrochelate iron(III) complex *via* oxidation of $FeDm_3(BF)_2$ clathrochelate with bromine, iodine, hydrogen peroxide, oxygen, cerium(IV), and copper(II) led either to obvious decomposition of the complex or to no reaction [47]. The macrobicyclic $FeDm_3(BF)_2$ complex was also obtained by the interaction of the initial Tchugaev type $Fe(HDm)_2Py_2$ bis-dimethylglyoximate with an excess boron trifluoride etherate in *n*-butanol [50]:

$$Fe(HDm)_2Py_2 + \text{excess } BF_3 \cdot (C_2H_5)_2O \xrightarrow{-Fe^{2+}} FeDm_3(BF)_2 \quad (11)$$

Acidic medium is also needed for efficient synthesis of $FeDm_3(BOR)_2$ complexes by Reaction 10. Therefore, $Na_2B_4O_7 \cdot 10H_2O$ and sodium and ammonium acetates, used for neutralization of the reaction mixture, were added in small amounts to increase the product yield. The use of $Na_2B_4O_7 \cdot 10H_2O$ as a capping agent instead of boric acid leads to no desired complexes [47].

The macrocyclization has been accelerated by heating the reaction mixture in a flask fitted with a reflux condenser. With alkoxy-containing complexes, care must be taken since upon inefficient cooling low-boiling boric acid esters can be distilled off, whereby the product yield is drastically reduced. In some cases, an appreciable effect has been observed when the water from the reaction mixture has been distilled off as azeotrope [47]. The preformed $FeDm_3(BOH)_2$ complex has undergone esterification in alcohol medium to give alkoxyboron-capped macrobicyclic compounds. Compounds of this type can also arise from transesterification of preformed complexes (Scheme 6) [47].

Transesterification of alkoxy-groups in macrobicyclic tris-dioximates is a modification reaction whereby the compounds that cannot be readily prepared by conventional methods may be




**Scheme 6**

synthesized. Thus, a clathrochelate $FeNx_3(BOC_6H_5)_2$ resulted from esterification of an initial $FeNx_3(BOH)_2$ complex in boiling phenol [49].

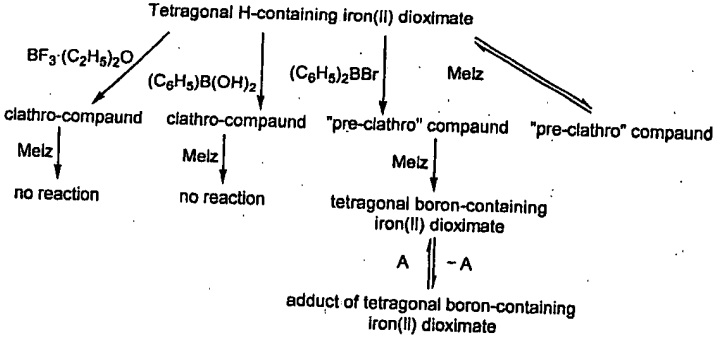
A route similar to Reaction 10 was utilized to prepare alkoxyboron-capped macrobicyclic $FeAd_3(BOR)_2$ and $FeBd_3(BOR)_2$ acetylacetonedioximates and α-benzyldioximates [51].

When phenylboronic acid was employed as a capping agent, a template condensation in methanol yielded an insoluble macrobicyclic $FeDm_3(BC_6H_5)_2$ dimethylglyoximate [52].

Attempts to synthesize $FeDm_3(BCl)_2$ and $FeDm_3(BBr)_2$ complexes were not successful, presumably due to reactions of capping $BCl_3$ and $BBr_3$ agents with the solvent [52]. It is rather intriguing that sodium borohydride has been used for preparation of hydride-containing tris-dioximate complexes. A prolonged reaction of iron(II) bromide, dimethylglyoxime, and $NaBH_4$ in anhydrous acetonitrile followed by recrystallization resulted in a macrobicyclic $FeDm_3(BH)_2$ complex containing a non-reactive B–H bond [52].

A methylboron-capped $FeBd_3(BCH_3)_2$ α-benzyldioximate was obtained *via* a direct reaction between iron(II) salt, α-benzyldioxime, and methylboronic acid in boiling *n*-butanol [52]. The fluoroboron-capped $FeBd_3(BF)_2$ α-benzyldioximate has been prepared both by a template condensation on the $Fe^{2+}$ ion [50] and *via* reaction of the preformed $Fe(HBd)_2(Melz)_2$ and $Fe(HBd)_2Py_2$ bis-dioximates with $BF_3{\cdot}(C_2H_5)_2O$ in diethyl ether or *n*-butanol [50, 53]. Reaction of the iron(II) bis-α-benzyldioximate with phenylboronic acid was also employed for the synthesis of a $FeBd_3(BC_6H_5)_2$ complex. The preparation of the tetragonal boron-containing iron(II) dioximates is possible with suitable (e.g., diarylsubstituted) boron-containing cross-linking reagents (Scheme 7) [53]. When diphenylboron bromide has been used as a reagent, boron-containing tetragonal bis-dioximates






**Scheme 7**

have been formed through "pre-clathro" intermediates that show a tendency to rearrange into a clathrochelates after a prolonged time. The "pre-clathro" compounds were isolated only in the case of weak cross-linking agents (e.g., $(C_6H_5)_2BBr$ and $(CH_3)_2BBr$) [53].

When macrobicyclic iron(II) dimethylglyoximates and α-benzyldioximates are studied in detail, for acyclic dioximes such as glyoxime, methylglyoxime, phenylglyoxime, and α-furyldioxime, only fluoroboron-, alkylboron-, and arylboron-capped complexes have been obtained by direct template condensation on the $Fe^{2+}$ ion and by interaction of the corresponding $Fe(HD)_2Py_2$ bis-dioximates with $BF_3{\cdot}(C_2H_5)_2O$ in *n*-butanol [21, 50].

Clathrochelate iron(II) complexes derived from alicyclic dioximes (nioxime, heptoxime, 4-methylnioxime, and octoxime) are of particular interest. The first clathrochelate $FeNx_3(BOH)_2$ and $FeNx_3(BF)_2$ compounds of this type, prepared by template cross-linking of three dioxime molecules on the $Fe^{2+}$ ion with a boric acid in water and $BF_3{\cdot}(C_2H_5)_2O$ in *n*-butanol, respectively, were described in Ref. 40. The syntheses with alicyclic dioximes have been realized for a number of boron-containing cross-linking agents in many cases, in a quantitative yield, and in dilute solutions well [49, 54-61].

Synthesis of the clathrochelate with hydridoboron capping groups *via* template condensation in dry acetonitrile occurs by Reaction 12:

$$FeBr_2 + 3H_2Nx + 2NaBH_4 \xrightarrow[AN]{} FeNx_3(BH)_2 + 2NaBr + 6H_2 \qquad (12)$$

to give a chromatographically isolated $FeNx_3(BH)_2$ complex [52, 58]. A nonmacrocyclic protonated $[Fe(H_2Nx)_3]Br_2$ tris-complex was obtained as an intermediate in the synthesis of this hydride-containing

clathrochelate. Interaction of this intermediate with $NaBH_4$ in THF also led to the formation of a clathrochelate $FeNx_3(BH)_2$ compound with a non-reactive B–H fragment. In contrast to tris(*iso*-propoxy)borane, this clathrochelate complex is inert in acetone even upon boiling for 16 h. Although acetoacetate is formed in some amount upon heating for 67 h in glacial acetic acid, the B–H fragments are partly retained. A similar result was obtained after 16 h treatment with concentrated hydrochloric acid at room temperature [58]. The use of substituted boron hydride, e.g., cyanboron hydride or sodium acetoanilidotrihydroborate instead of $NaBH_4$ in Reaction 12, resulted in no new compounds [52].

The alicyclic clathrochelate $Fe(4MNx)_3(BR)_2$ (where R is $CH_3$, *n*-$C_4H_9$, $C_6H_5$, OH, O*iso*-$C_3H_7$, O*n*-$C_4H_9$, O*sec*-$C_4H_9$, F); and $FeGx_3(BR)_2$ and $FeOx_3(BR)_2$ (where R is $CH_3$, *n*-$C_4H_9$, $C_6H_5$, OH, $OCH_3$, O*n*-$C_4H_9$, and F) tris-dioximates have been synthesized in the same manner as the corresponding nioximates [59-61]. Since alkoxyboron-capped iron(II) 4-methylnioximates do not readily crystallize from organic solvents, with lower alcohols ($CH_3OH$ and $C_2H_5OH$) the alkoxyde complexes were not isolated as solids [59].

With the majority of alicyclic boron-capped iron(II) dioximates, neither template condensation nor recrystallization from organic solvents gave crystals suitable for X-ray analysis. A rate-controlled template condensation within several days yielded $FeGx_3(BOH)_2 \cdot 3H_2O$ monocrystals, since the synthesis of this clathrochelate compound proceeds much more slowly than that of analogous complexes with nioxime and 4-methylnioxime [62, 63].

In most cases, the synthesis of macrobicyclic iron(II) tris-dioximates occurs *via* a one-step procedure, enabling one to obtain only complexes with identical dioxime fragments and capping groups. It is not expedient to utilize mixtures of dioximes or capping agents with similar properties in these processes to produce meridional ($C_3$) and axial ($C_2$) nonsymmetric compounds, respectively, because of the formation of a mixture of products that is close to a statistical one. The predominant formation of the symmetric complexes has been observed even when the dioximes and capping agents used differ significantly in their properties. In the case of dioximes, this can be accounted for by the difference in the stability constants of nonmacrocyclic tris-dioximates as first intermediates (for example, $\beta_3^{[Fe(H_2D)_3]^{2+}} >> \beta_3^{[Fe(H_2D)_2(H_2D')]^{2+}}$, see Chapter 4). The predominantly formed symmetric $[Fe(H_2D)_3]^{2+}$ complex reacts with cross-linking



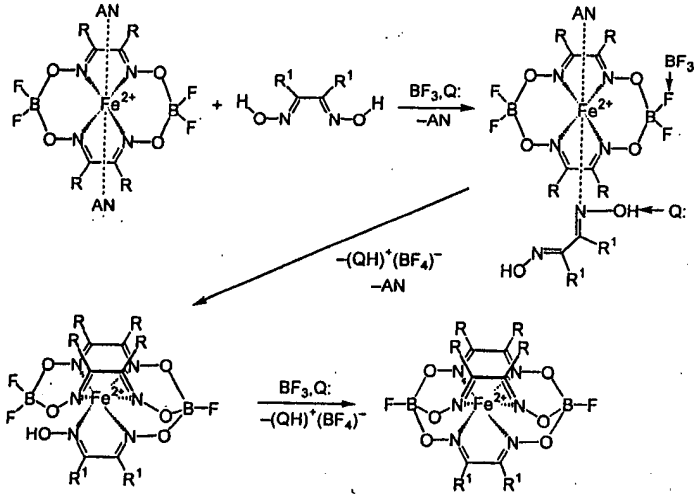
agents owing to the symmetric clathrochelate product. Similarly, in the case of capping agents, when the capping agents display an essentially different activity, a second (semiclathrochelate) intermediate, will be formed preferentially by the more efficient agents and will presumably be capped in a statistical ratio, since the second capping is not a rate-controlling step (see Chapter 4). Additionally, a higher crystal lattice energy of symmetric compounds compared with that of nonsymmetric ones is observed: in most cases clathrochelates are obtained as solids in the course of the reaction, and, therefore, an increase in the crystal lattice energy leads to a shift in equilibrium in the direction of the symmetric product. When $C_2$-nonsymmetric dioximes such as phenylglyoxime or methylglyoxime are employed as the initial ligand, a mixture of *fac*- and *mer*-isomers has been formed. In spite of the fact that clathrochelates are produced by a multistage mechanism through the formation of a semiclathrochelate in all cases except one (see below), the semiclathrochelates have not been isolated because of their lability. At the same time, a directed synthesis of clathrochelates containing different dioximate fragments and capping agents allows one to produce reactive precursors suitable for further functionalization, as well as to vary rather finely the physicochemical properties of the products obtained [64].

$C_3$-nonsymmetric iron(II) clathrochelates have been obtained by the cycloaddition of α-dioximes to initial square-planar macrocyclic iron (II) bis-dioximates by the Reaction 13:

$$[FeD_2(BF_2)_2AN_2] + H_2D' \longrightarrow FeD_2D'(BF)_2 + 2\,HF \qquad (13)$$

It is obvious that this reaction is favored by binding the HF acid released during its course, i.e., in the presence of $H^+$ and $F^-$ ion acceptors. A weakly coordinating sterically hindered N,N-di(*iso*-propyl)ethyl amine and boron trifluoride etherate have been used as $H^+$ ion acceptor and electrophilic agent to remove $F^-$ ions, respectively. In addition, $BF_3 \cdot O(C_2H_5)_2$ has prevented the side fluoroboron caps elimination reaction (Scheme 8).

The cycloaddition reaction proceeds under more rigid conditions and takes more time than a direct template condensation on the iron(II) ion. This can be explained by the fact that the overall mechanism of clathrochelate synthesis involves an intermediate tris-complex formation step. It is evident that macrocyclic square-planar iron(II) bis-dioximates are relatively kinetically stable, and the



Scheme 8

addition of a third dioxime molecule involves not only detachment of an axially coordinated solvate molecules, but also considerable changes in the iron(II) ion coordination arrangement.

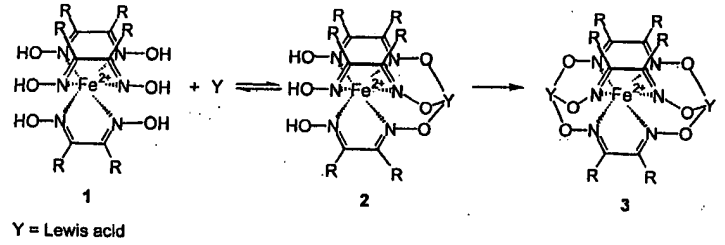
In the absence of $F^-$ ion acceptors, a clathrochelate is not formed and the reaction completed at a stage of *cis*-addition of the protonated dioxime to a square-planar macrocycle. With certain dioximes ($H_2Nx$ and $H_2Dm$), in the absence of the base the reaction yields a mixture of symmetric clathrochelates. In other cases, only a mixture of decomposition products has been formed [64].

A direct synthesis of $C_2$-nonsymmetric tris-dioximate iron (II) lathrochelates *via* the formation of semiclathrochelate complex **2** cannot be realized even with a great excess of complex **1**, since compound **2** readily disproportionates to give **1** and **3** (Scheme 9).

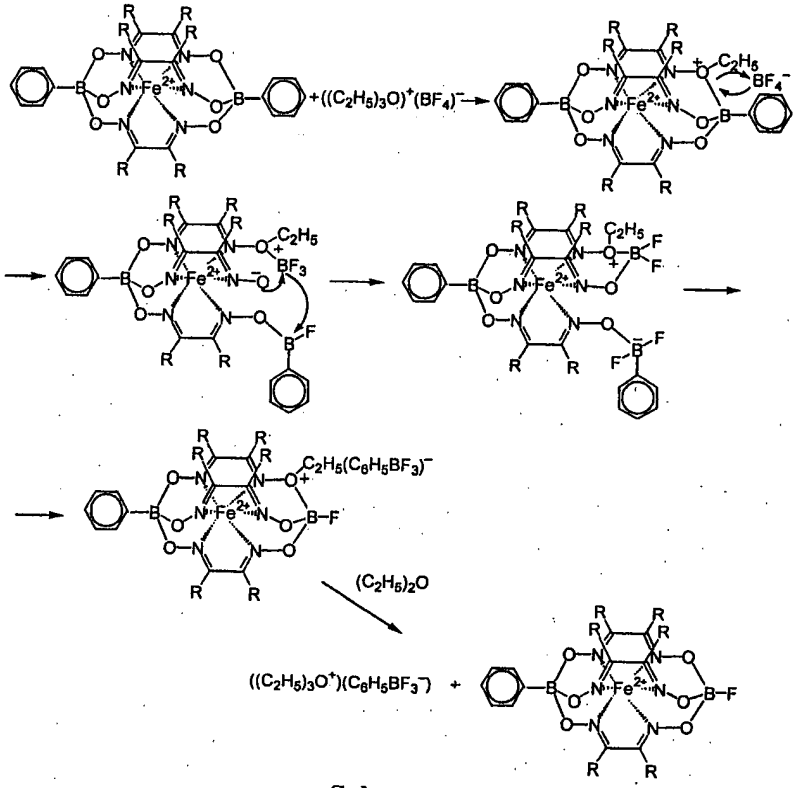
A $C_2$-nonsymmetric $FeNx_3(BC_6H_5)(BF)$ complex was obtained *via* a "re-boronating" reaction from the initial $FeNx_3(BC_6H_5)_2$ clathrochelate attacked by triethyloxonium boron fluoride, and the complex obtained was chromatographically isolated (Scheme 10).

However, this is not a general method; attempts to prepare the $FeDm_3(BC_6H_5)(BF)$ complex by an analogous scheme have not been

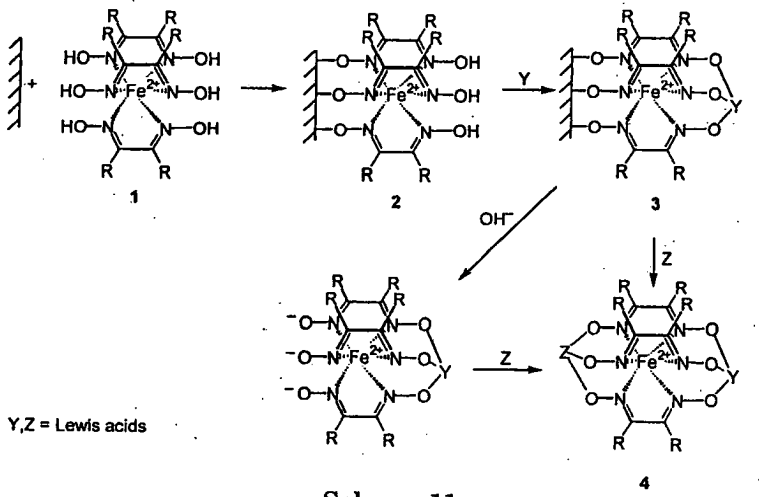




Scheme 9



Scheme 10




**Scheme 11**

successful (only a symmetric $FeDm_3(BF)_2$ complex has been formed) [64].

The synthesis of $C_2$-nonsymmetric clathrochelate iron(II) dioximates was realized through a stepwise "assembling" on the sorbent surface (Scheme 11).

A chemical immobilization of a nonmacrocyclic tris-complex **1** on the matrix surface has enabled one to protect one of the two triangular planes formed by the oxime group (**2**) and to obtain the immobilized semiclathrochelate **3** *via* cross-linking with Lewis acids. The desorption of these semiclathrochelates with the help of another capping agent leads to the formation of $C_2$-nonsymmetric clathrochelate **4**. The success of the synthesis carried out by this procedure is governed by a sorbent aptitude for a specific binding of the initial tris-complex **1** and the subsequent desorption of a semiclathrochelate **3** affected by cross-linking agents.

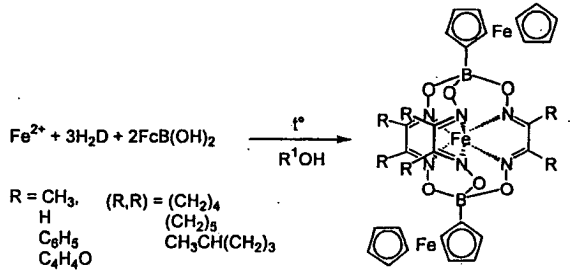
The best results were obtained with aluminium hydroxide resulting from hydrolysis of aluminium(III) *iso*-propylate. A high sorption capacity (*ca* 10%) of compound **2**, a high degree of desorption of complex **3**, and the purity of the resulted clathrochelate **4** make aluminium(III) hydroxide the most suitable matrix for the synthesis of targeted compounds [64].



The unique properties of a metal ion encapsulated in the cage of a macropolycyclic ligand and isolated from the influence of external factors have allowed the use of clathrochelates as models of important biological systems, electron carriers, and catalysts of photochemical and redox processes (see above). However, the low reactivity of the majority of the clathrochelates impedes their modification and hence the possibility of their utilization for the solution of these problems.

An apical functionalization of clathrochelates enables one to obtain complexes with improved chemical, physicochemical, biomimetic, and bioactive properties and characteristics that are primary governed by functionalized groups [65]. The possibility of an apical modification of macrobicyclic α-dioximates and oximehydrazonates is indicated by the relative availability of functionalized boron-containing Lewis acids as efficient capping agents.

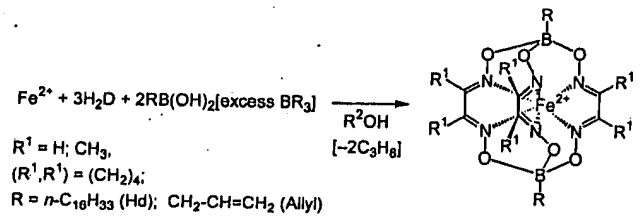
Ferrocenylboron-capped macrobicyclic iron(II) acyclic, alicyclic and aromatic dioximates as potential electron carriers were synthesized by direct template reactions using ferrocenylboronic acid as the cross-linking agent [66].




(14)

The introduction of lipophilic substituents is of interest for producing surface-active compounds (surfactants) and liquid-crystal systems. The complexes with allyl substituents at the apical boron atoms are precursors for the synthesis of linear and netlike polymeric clathrochelates.

Clathrochelate iron(II) tris-dioximates with hexadecylboron capping groups were synthesized by direct template condensation of acyclic and alicyclic dioximes with the corresponding $n$-$C_{16}H_{33}B(OH)_2$ boronic acid (denoted as $HdB(OH)_2$) on iron(II) ion in methanol:



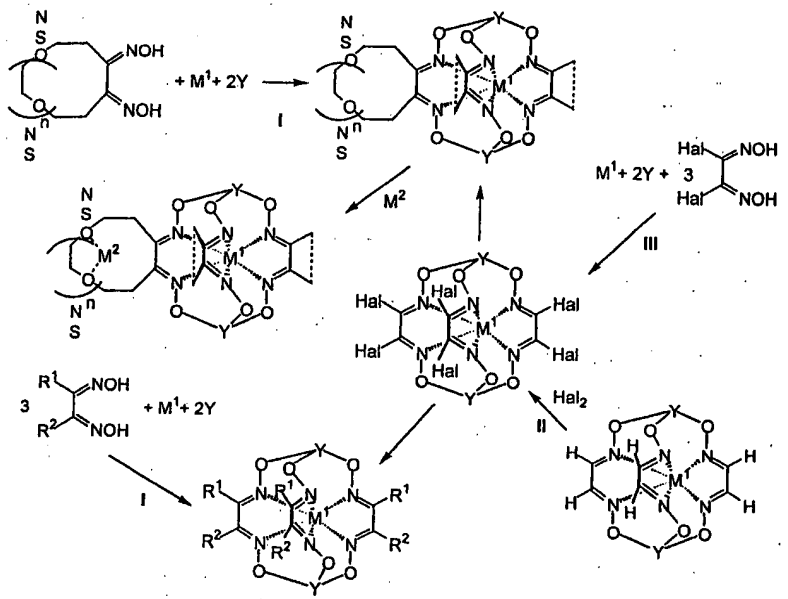

(15)

Allylboron-capped compounds were prepared similarly in *n*-butanol using triallylborane $BAllyl_3$ instead of $HdB(OH)_2$. Under these reaction conditions, two of the three B–C bonds in $BAllyl_3$ are cleaved by *n*-butanol or water to form $AllylB(OH)_2$ and propane [67].

The mutual electronic influence of the apical substituents and the clathrochelate framework (and, therefore, the encapsulated ion) is negligible. The steric effects of apical substituents are also small. The substituents in chelating (ribbed) fragments of polyene clathrochelates have much greater steric and electronic effects on the coordination polyhedron geometry and the central metal ion properties because of the direct interaction of the $\pi$-system of a ligand and the $\pi$- and $\sigma$-system of a substituent. As a result, one has an opportunity to use such substituents in order to change the central metal ion characteristics; conversely, one can change the central metal ion configuration *via* a redox transition to affect the electronic characteristics of substituents. From this point of view, the synthesis of ribbed-functionalized clathrochelates with substituents apt to coordinate a metal ion to produce polynuclear complexes with interaction through the clathrochelate framework metal centers is of particular interest: polynucleating ligand systems and polynuclear complexes of *d*-metals derived from them are actively being investigated as models of metalloproteins and metalloenzymes and other important biological systems (biomimetics), efficient catalysts for chemical reactions, and promising materials for molecular electronics (molecular magnets, switches, transistors, and wires) [65].

The most feasible Routes I-III for the synthesis of triribbed-functionalized α-dioximate clathrochelates (Scheme 12) were proposed in Ref. 65. The halogen-carbon bonds are reasonably active in nucleophilic substitution reactions, and the dihalogenoxime complexes are relatively stable (unlike dihalogenoximes, these complexes are available and undergo no intramolecular conversions






**Scheme 12**

that could complicate modification reactions). It is rather complicated to use the preliminarily functionalized α-dioximes (Route I) in the synthesis of clathrochelates to obtain partially substituted compounds and complexes with redox-active coordinating groups. In the course of a template condensation on the metal ion, the preliminarily functionalized α-dioximes can react not only with oxime groups but also with functionalizing substituents. Side reactions of these groups can markedly reduce the yield of the desired products and hinder their isolation. Consequently, Routes II and III (Scheme 12) were chosen for the synthesis of the ribbed-functionalized clathrochelates. Route II has been regarded as the most promising procedure since modern methods for the synthesis of the initial glyoximate clathrochelates with yields of 70 to 80% are

developed. However, attempts to implement a complete halogenation of dioximate fragments of such complexes and to isolate hexahalogenide precursors of triribbed-functionalized clathrochelates has met with failure. A mixture of partial substitution products, largely containing trihalogen-substituted compounds, was obtained. In addition, in the case of a phenylboronic $FeGm_3(BC_6H_5)_2$ glyoximate the halogenation side reactions of the aromatic substituents at apical boron atoms were observed [65].

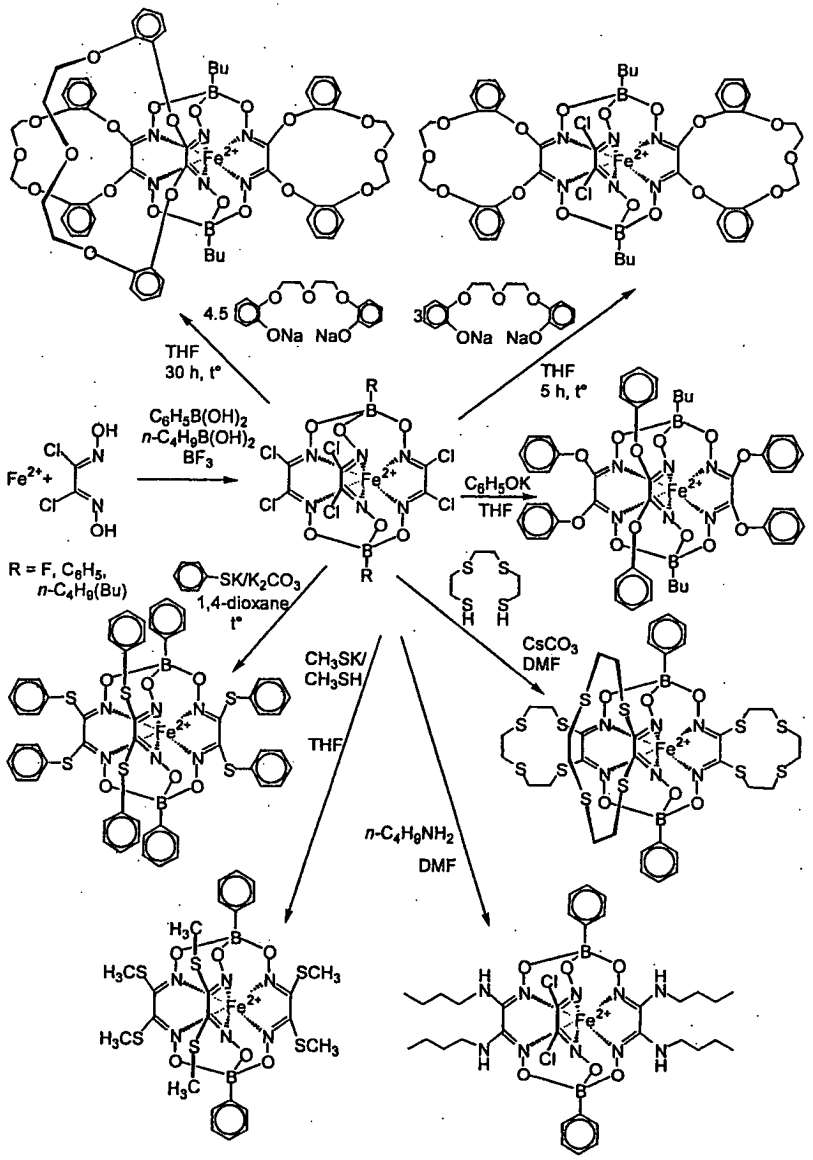
The use of Route III presented problems because the attempts to obtain hexahalogenide precursors from initial dihalogendioximes by the standard procedures of synthesis of such clathrochelates have not been successful. Nevertheless, the conditions under which the yield of these complexes was 60-90 % were selected in Ref. 65: nitromethane was as a solvent, and acetonitrile $FeAN_4Cl_2$ solvato-complex as a source of $Fe^{2+}$ ions, and the water was removed from the reaction mixture. The three hexachloride precursors with phenylboronic, *n*-butylboronic, and fluoroboronic capping groups (Scheme 13) were obtained [65].

Hexachloride precursors interacted with excess thiophenol in the presence of potassium carbonate under soft conditions to yield hexathiophenol clathrochelates (Scheme 13).

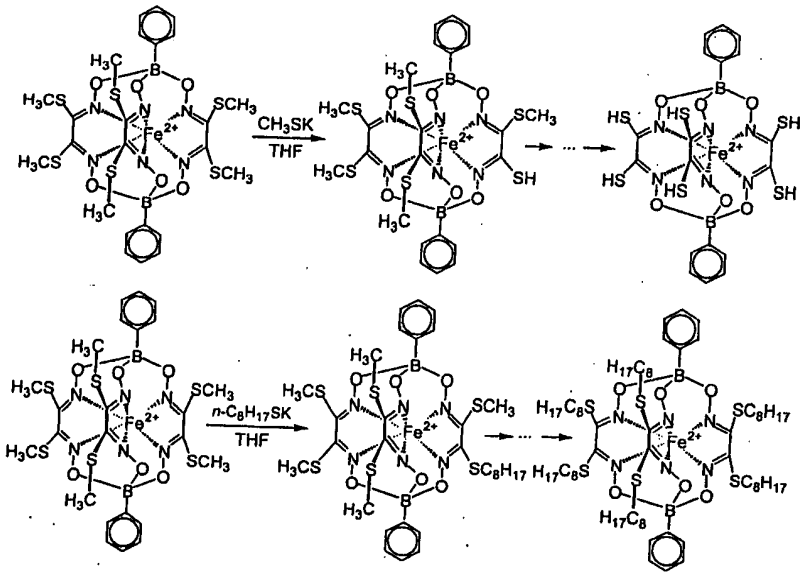
The reaction with an excess of methylmercaptan in the presence of potassium carbonate at room temperature led to the formation of partially substituted products only, mainly trisubstituted clathrochelates. Therefore, a more active potassium methylmercaptanate was used in the synthesis of the hexasubstituted product, and the reaction readily proceeded in a high yield [65].

The thioalkyl-containing macrobicyclic complexes have been dealkylated and realkylated easily under the action of potassium thiolates in aprotonic media (Scheme 14). The products of de- and realkylation reactions were detected by PD and FAB mass spectrometry. In this respect the thioalkyl-containing clathrochelates are close to the aryl alkyl sulfides. In the course of thioalkyl derivative synthesis with an excess of potassium thiolate, a mixture of dealkylated products was obtained in addition to the desired hexathioalkyl clathrochelates. The addition of corresponding alkyl iodide and potassium carbonate to the reaction mixture in the final stage of reaction led to an increase in yields by alkylation of HS groups, resulting in the side dealkylation process [65].






**Scheme 13**



**Scheme 14**

The reaction of a *n*-butylboronic precursor with potassium phenolate led to the formation of hexaphenol $Fe((C_6H_5O)2Gm)_3(Bn\text{-}C_4H_9)_2$ complex (Scheme 13). Attempts to obtain of the *n*- and *t*-butoxy-containing clathrochelates met with failure because of the destruction of precursors.

The well-known synthetic procedures for crown ethers and their analogs allowed one to synthesize clathrochelates with dioximate fragments of the oxo- and thioether crown type (Scheme 13). The interaction of phenylboronic and *n*-butylboronic precursors with 3 mols of the sodium salt of bis-(2-(*o*-oxyphenoxy))diethyl ether for 5 h in THF at 50-60° led largely to the formation of $C_3$-nonsymmetric tworibbed-substituted products (Scheme 13). The reactions of *n*-butylboronic precursor were studied in more detail. The use of a 30% excess of the sodium salt of bis-(2-(*o*-oxyphenoxy))diethyl ether and an increase in the reaction time up to 30 h permits one to isolate a tricrown ether clathrochelate (Scheme 13). Tetrabutylammonium salt $((n\text{-}C_4H_9)_4N)Cl$ was used as an interphase catalyst for the



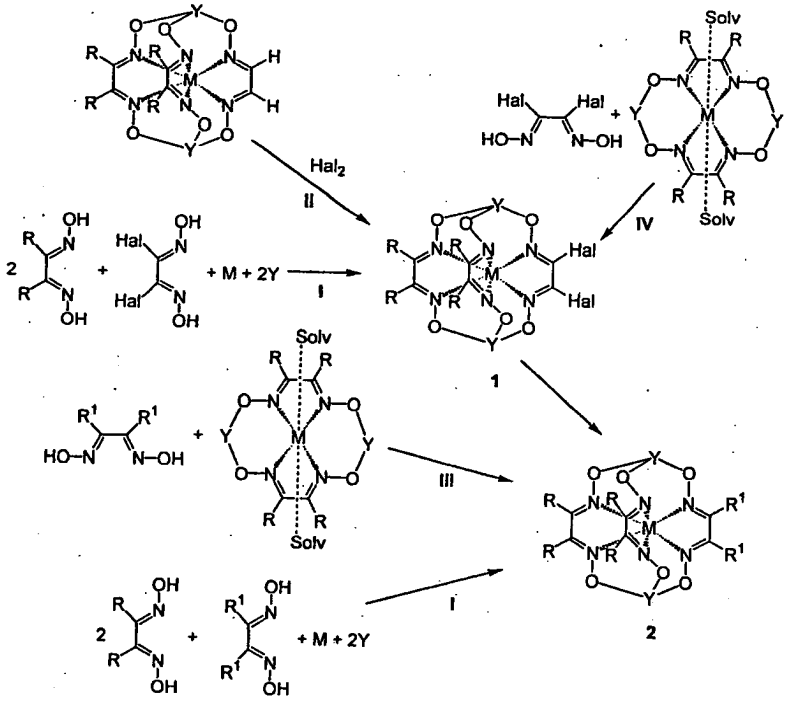
condensation reaction. The by-products of this reaction mainly resulted from the condensation reaction of one of the two deprotonated oxy groups of bis-(2-(*o*-oxyphenoxy))diethyl ether and the dichloroglyoximate fragments of the precursor. Such open-chain compounds are readily soluble in methanol. Attempt to use the sodium triflate at a high concentration and to create the appropriate conditions for a template condensation on the sodium ion through orientation of the terminal oxygen atoms met with failure [65].

The template condensation of *n*-butylboronic precursor with 3,5-dithiaoctane-1,8-dithiol in the presence of $Cs_2CO_3$ allowed to obtain in a low yield tris-(12-an-$S_4$)-containing clathrochelate as a representative of a promising series of models of "blue" proteins [65].

The appropriate conditions for the synthesis of tris-azamacrocyclic clathrochelates containing dioximate fragments in polyazamacrocyclic rings were not selected. Attempts to use open-chain polyamines, as well as their complexes with transition metals, primarily $Ni^{2+}$, gave no desired results.

The reaction of a phenylboronic precursor with an excess of *n*-butylamine unexpectedly led to the preferential formation of the tetrasubstituted clathrochelate by the modification of two of the three dichloroglyoximate fragments (Scheme 13). A similar product was also obtained in the case of cyclohexylamine. Attempts to obtain a hexa-*n*-butylamine clathrochelate were not successful. The interaction of precursors with aniline and its derivatives has resulted in the formation of a mixture of di- and trisubstituted products, which failed to be isolated as individual compounds [65].

Clathrochelate ribbed-functionalized tris-dioximates have attracted interest because they offer scope for the synthesis of polynuclear complexes with targeted structural parameters and physicochemical properties (see above). In most instances, it is not necessary to functionalize all α-dioximate fragments, and it appears to be sufficient to modify only one of the three ribs in the clathrochelate framework to alter the properties significantly. Several feasible synthetic routes to clathrochelate monoribbed-functionalized tris-dioximates have been proposed in Ref. 68. A direct template condensation of the mixture of α-dioximes with Lewis acids on a metal ion (Scheme 15, Route I) leads to the formation of a poorly separable mixture of nonsymmetric and symmetric products, in which the latter predominate. Halogenation of the initial clathrochelate




R=aliphatic or aromatic substituent; (R,R)=alicyclic fragment
$R^1$=functionalizing substituent; ($R^1$,$R^1$)=crown etheric or another macrocyclic fragment
Y=Lewis acid

**Scheme 15**

monoglyoximate (Scheme 15, Route II) is complicated, since by-products are readily generated from partial halogenation of a glyoximate moiety and aliphatic and aromatic substituents in two other dioximate fragments as well. The methods of preparation developed for $C_3$-nonsymmetric clathrochelates (see above) may be used for the synthesis of desired tris-dioximates **1** and **2** from square-planar macrocyclic bis-dioximates and are thought to be the most promising ones (Scheme 15, Routes III and IV). Route III makes use of the condensation of the functionalized α-dioxime with the macrocyclic bis-dioximate. However, the appearance of additional coordinating groups and side reactions associated with



functionalising substituents drastically reduces the desired product yield. Route IV at the first stage produces a reactive dihalogenide precursor that readily undergoes modification by well-known procedures (Scheme 16). This route was chosen for the synthesis of a series of monoribbed-functionalized clathrochelate iron(II) dioximates [68]. The synthesis of the dichloride precursor was implemented from dichloroglyoxime and macrocyclic iron(II) $FeBd_2(BF)_2)_2AN_2$ bis-α-benzyldioximate. Last complex was chosen as the starting compound because of its availability and relative stability to a side reaction of disproportionation to yield a symmetric $FeBd_3(BF)_2$ clathrochelate as by-product [68].

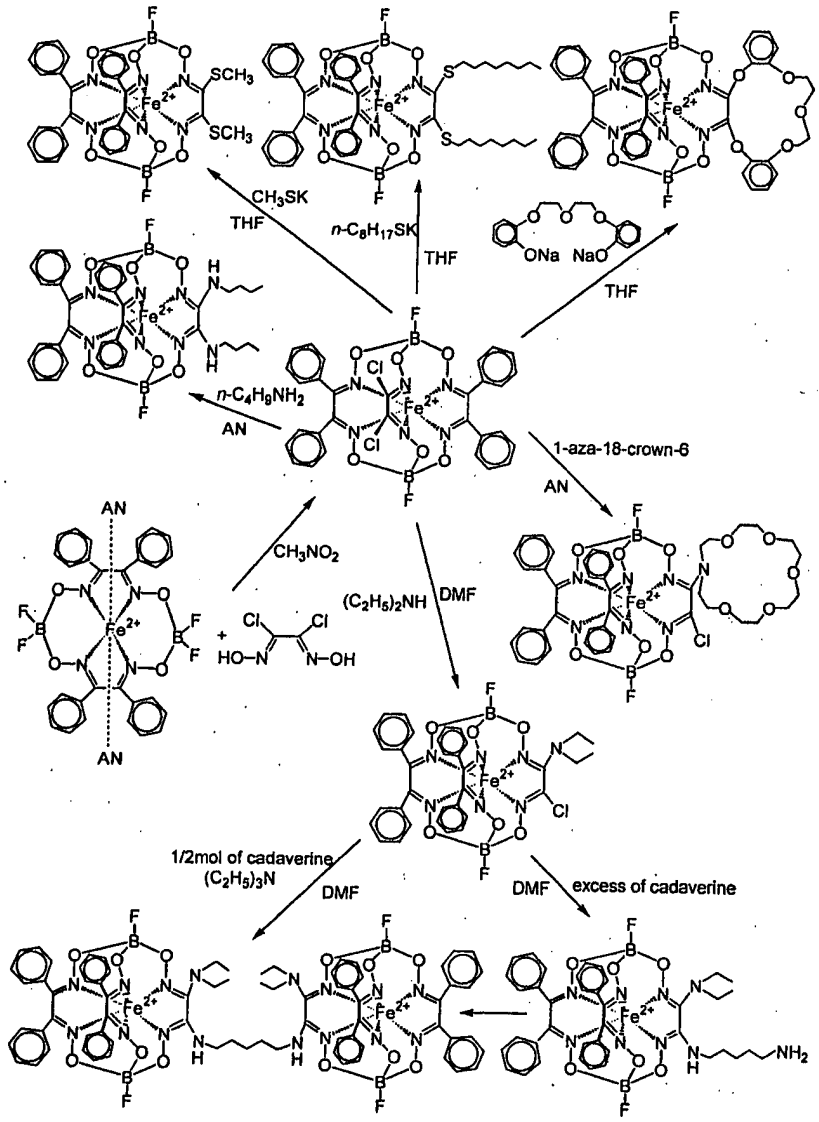
The dichloride precursor readily reacted with sterically unhindered primary amines to form disubstituted products (Scheme 16).

Secondary amines underwent a reaction that involved the substitution of only one of the two chlorine atoms. The reaction of precursor $FeBd_2(Cl2Gm)(BF)_2$ with an excess of *aza-18-C-6* and diethylamine resulted in the formation of the monocrown-substituted $FeBd_2$((aza-18-C-6)ClGm)$(BF)_2$ clathrochelate and the monodiethyl-amine-containing $FeBd_2((((C_2H_5)_2N)ClGm)(BF)_2$ complex. An attempt to isolate the corresponding disubstituted complexes was not successful. These monofunctionalized complexes may undergo further functionalization, especially with primary aliphatic amines. The use of primary aliphatic diamines allows one to obtain the functionalized spacer-containing $FeBd_2((((C_2H_5)_2N)(NH(CH_2)_5NH_2)Gm)(BF)_2$ clathro-chelate and $(FeBd_2((((C_2H_5)_2N)Gm)(BF)_2)_2(NH(CH_2)_5NH)$ bis-clathro-chelate [68].

The synthesis of the functionalized macrobicyclic $FeBd_2(CwGm)(BF)_2$ compound containing one crown ether dioximate fragment was carried out using the approach proposed for triribbed-functionalized clathrochelates (see above).

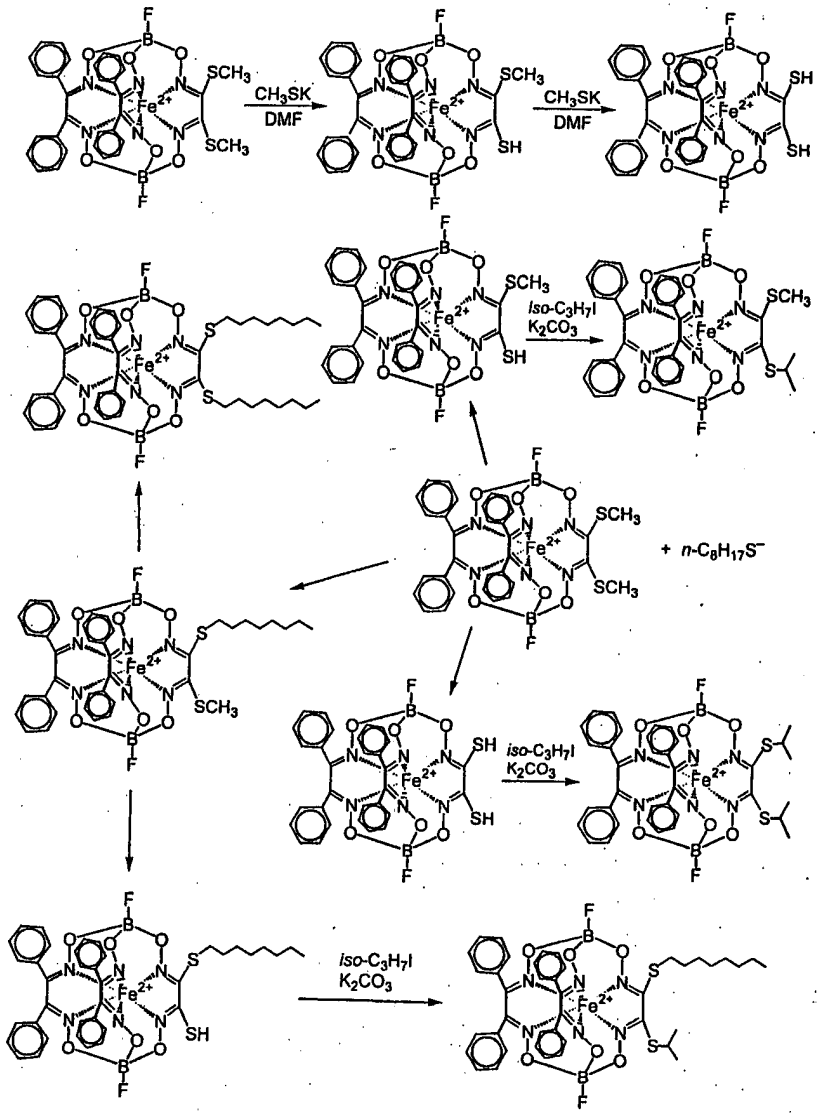
Reaction of the $FeBd_2(Cl2Gm)(BF)_2$ precursor with potassium aliphatic thiolates such as $CH_3SK$ and *n*-$C_8H_{17}SK$ was complicated by side reactions of stepwise dealkylation of the resulting products in an excess of the thiolate ion. For the methylthiol $FeBd_2((CH_3S)2Gm)_2(BF)_2$ complex, this process occurred most readily.

This clathrochelate also readily underwent de- and realkylation, especially with *n*-octylthiolate ion in DMF (Scheme 17) like the triribbed-functionalized clathrochelates. The purification can be improved and the yield of the desired product increased by the




Scheme 16






Scheme 17

addition of the corresponding alkyl iodide at the final stage of this process [68].

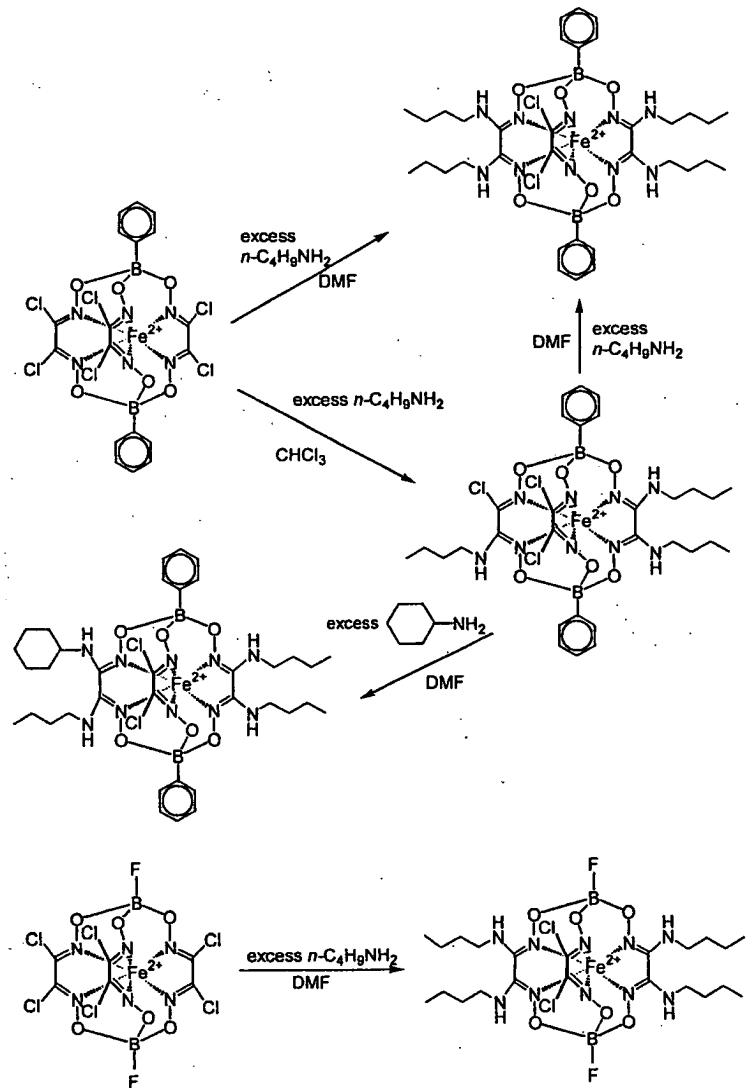
A systematic study of the effect of both aliphatic amines and the nature of the solvent on the products of reactions with reactive di- and hexachloride clathrochelates was performed [69].

The reactions of phenyl-, *n*-butyl- and fluoroboron-capped hexachloride iron(II) precursors with aliphatic amines proceeded under steady-state conditions of the solvent, temperature, and reaction time to produce clathrochelates of only one type irrespective of the nature of the substituent at the boron atom (Scheme 18). Therefore, the reactions of the phenylboronic $Fe(Cl2Gm)_3(BC_6H_5)_2$ precursor were studied. The reaction of precursor with *n*-butylamine in DMF, benzene, THF, and *n*-butylamine as the solvent led to the formation of only tetrasubstituted clathrochelate, whereas the reaction in chloroform unexpectedly resulted in trisubstituted clathrochelate, which underwent further functionalization in DMF with *n*-butylamine and cyclohexylamine but did not react with diethylamine (Scheme 18).

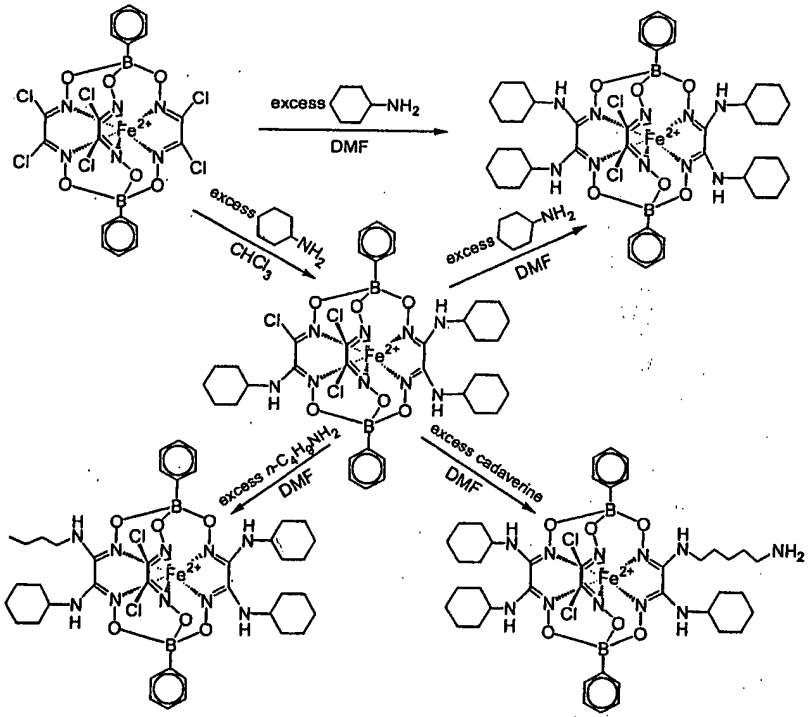
The reaction of phenylboronic precursor with primary alicyclic cyclohexylamine in DMF and $CHCl_3$ also led to the formation of tetra- and trisubstituted clathrochelates, respectively (Scheme 19). Trisubstituted clathrochelate underwent further functionalization in DMF with an excess of *n*-butylamine and aliphatic diamine (cadaverine). Thus, the overall reaction pathway in the previously mentioned reactions with primary sterically unhindered aliphatic amines involved a stepwise substitution in two of the three dichloroglyoximate fragments of hexachloride clathrochelates [69].

In the case of a sterically unhindered secondary aliphatic amine, in particular diethylamine, and of a sterically hindered *t*-butylamine, the reaction proceeded *via* a different pathway (Schemes 20 and 21). First, the reaction stopped at an earlier stage: trisubstituted and disubstituted clathrochelates were formed in DMF and $CHCl_3$, respectively. Second, in the case of *t*-butylamine, the reactions in chloroform and DMF gave di- and trisubstituted clathrochelates, respectively, with the substitution in two of the three dichloroglyoximate fragments (Scheme 20). But in the case of *t*-butylamine trisubstituted complex, together with substitution products in two of the three dioximate moieties, *fac*- and *mer*-isomers of this complex with *t*-butylamine substituents in three dioximate fragments were identified (Scheme 21). In the case of diethylamine,






**Scheme 18**

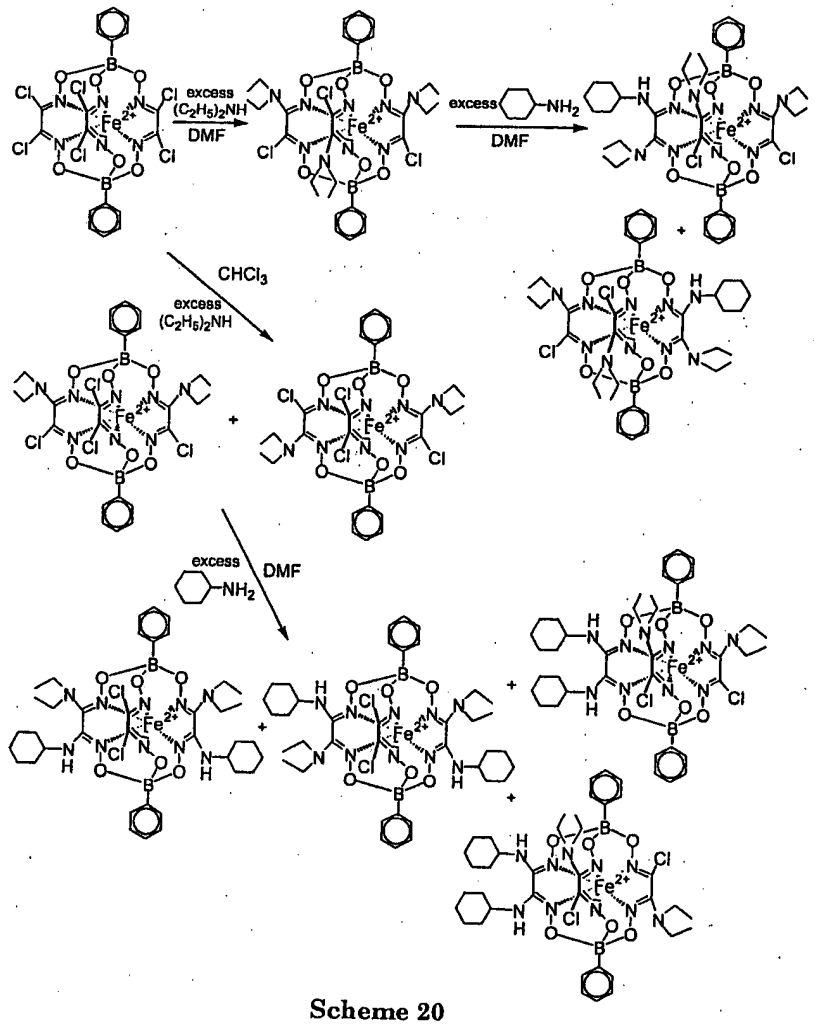



**Scheme 19**

only a *mer*-isomer of trifunctionalized clathrochelate with substitution in the three dioximate fragments was obtained (Scheme 20). The resultant clathrochelates underwent further modification with a more reactive amines (Schemes 20 and 21). Analogous trisubstituted clathrochelates were also obtained *via* the reaction of phenylboronic precursor with dimethylamine and morpholine in DMF, 1,4-dioxane, and THF [69].

Dichloride $FeBd_2(Cl2Gm)(BF)_2$ precursor readily reacted with aliphatic primary amines of different natures in the DMF and THF to produce disubstituted clathrochelates (Scheme 22). The secondary amines react with dichloride precursor to substitute one of the two reactive chlorine atoms, and this permits one to obtain spacer-containing clathrochelate and bis-clathrochelate (Scheme 23). An alternative pathway for the synthesis of bis-clathrochelates uses

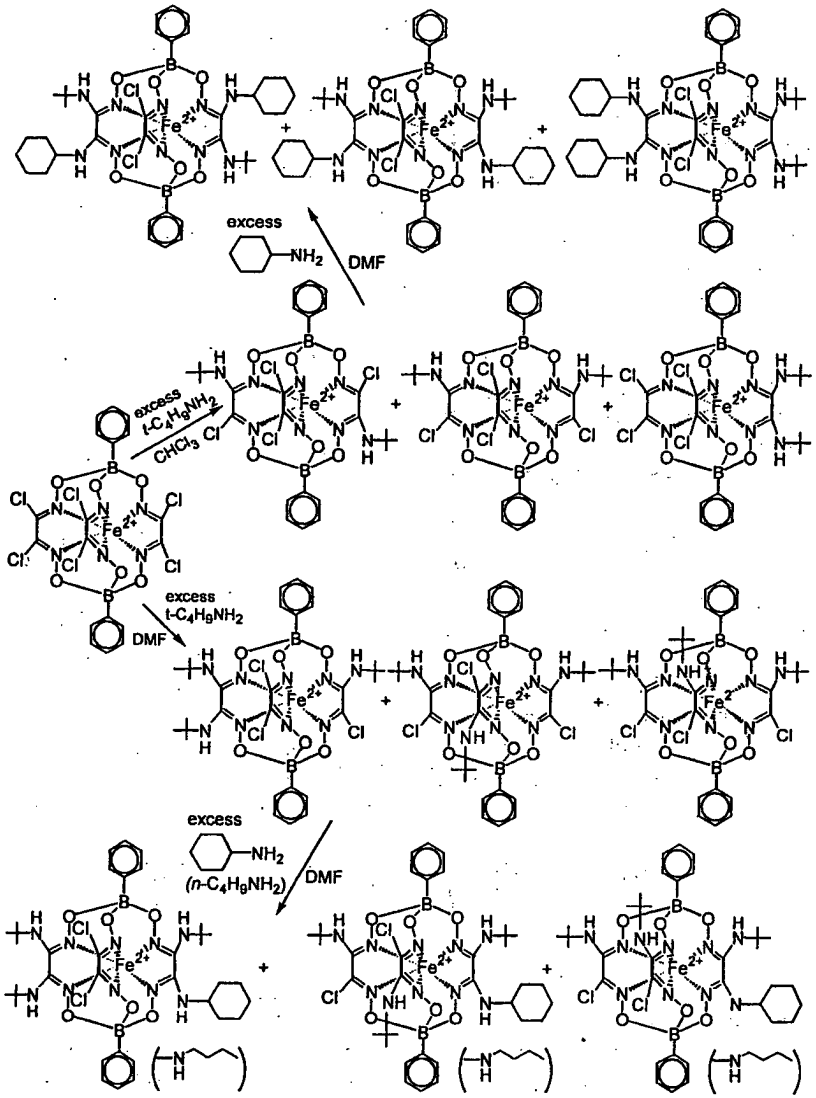





**Scheme 20**

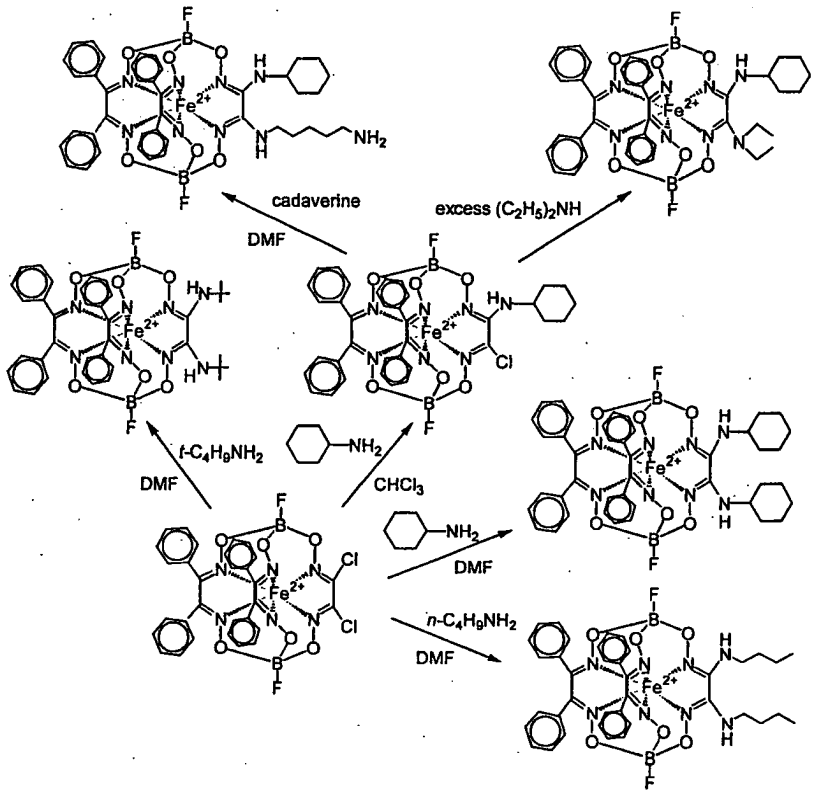
secondary diamines, in particular piperazine (Scheme 23). In this case, monosubstituted bis-clathrochelate has been formed in both DMF and chloroform.

The causes of such unexpected influences of the nature of both amines and solvents on the reaction products are discussed in Ref. 69.



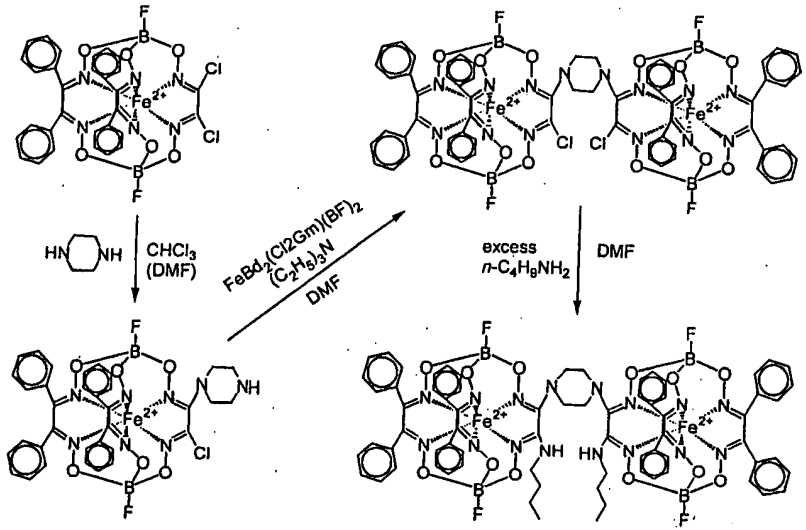

Scheme 21



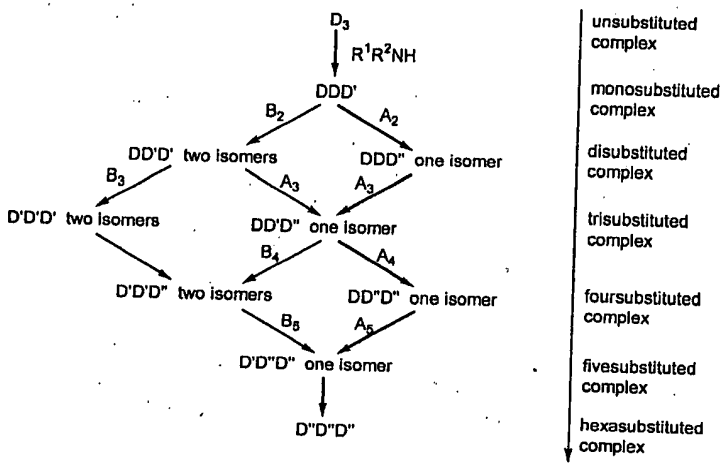



Scheme 22

The nucleophilic substitution of the reactive chlorine atoms in hexa- and dichloride clathrochelates by a series of aliphatic amines is very sensitive to the effects of the medium (primary, the solvent employed), and the trend of the reaction is determined to a great extent by the donor properties of the amines and the steric accessibility of the nucleophilic centre. The subsequent substitution reaction course and feasible reaction products in the case of hexachloride precursors are presented in Scheme 24. The stepwise-formed clathrochelate complexes are denoted according to the degree of the substitution of chlorine atoms by amine groups:




**Scheme 23**




**Scheme 24**



- D stands for a dichloroglyoximate fragment, $Cl2Gm^{2-}$;
- D' corresponds to a monosubstituted dioximate fragment, $(R^1R^2N)C1Gm^{2-}$;
- D" denotes a diamine fragment, $(R^1R^2N)2Gm^{2-}$.

According to Scheme 24, 12 reaction products can be formed. The following results were established:

1. The reactivity of partially substituted iron(II) clathrochelates is essentially dependent on the degree of substitution with primary sterically unhindered aliphatic amines in donor solvents. In the case of hexachloride precursors, a tetrasubstituted product is formed and is inert to further actions of amines.
2. Different chlorine-substituted fragments in partially substituted complexes have similar reactivities, and the direction of the reaction is not determined by the electron density on the carbon atoms (i.e., their electrophilic properties) but by more specific effects: an intramolecular activation *via* hydrogen bonds in the case of sterically unhindered primary amines and sterical hindrances in the case of secondary and sterically hindered primary amines. The reaction with sterically unhindered primary amines occurs *via* the route $\mathbf{A_n}$ through the substitution of a halogen atom from an already monofunctionalized fragment. In the case of secondary and sterically hindered primary aliphatic amines, the reaction proceeds *via* the route $\mathbf{B_n}$ with sterically controlled substitution.
3. The reactions of nucleophilic substitution with participation of reactive clathrochelates are very sensitive to the donor properties of an attacking amine. With aromatic amines, as well as secondary and primary sterically hindered amines in acceptor solvents, and hexachloride precursors, the reaction stops with the formation of disubstituted products. When secondary and sterically hindered primary aliphatic amines are used in donor solvents and sterically unhindered primary aliphatic amines in acceptor solvents, the reaction terminates at trisubstituted products. In the case of sterically unhindered aliphatic amines, tetrasubstituted clathrochelates are formed. With dichloride precursor $FeBd_2(Cl2Gm)(BF)_2$, the primary aliphatic amines in donor solvents form diamine clathrochelates, whereas the secondary amines (diethylamine or piperazine) give only monoamine complexes both in acceptor and donor solvents.

In the case of primary aliphatic amines, the reaction products are dramatically affected by the solvent employed. For instance, in the presence of solvents apt to produce a specific solvation of amines (chloroform, and an amine chlorohydrate solution in methylene dichloride), the reaction with hexachloride precursors terminates to yield the trisubstituted product DD'D" formed *via* route A. At the same time, the use of some other solvents (such as benzene, 1,4-dioxane, THF, methylene dichloride, DMF, and alcohols, or the corresponding amine media) led to the formation of the sole tetrasubstituted product (DD"D"). In addition, in the case of sterically unhindered primary amines an alternative isomer (D'D'D") is not isolated, which indicates reaction route A and a specific control of the tie reaction in the transition state by solvation interactions and intramolecular hydrogen bonds. In the case of the dichloride $FeBd_2(Cl2Gm)(BF)_2$ precursor, with both primary (cyclohexylamine) and secondary (diethylamine and piperazine) aliphatic amines, only a monosubstituted product of the $Bd_2D'$ type is formed in chloroform, whereas in some other solvents, a diamine clathrochelate of the $Bd_2D"$ type is obtained with both sterically hindered and unhindered primary aliphatic amines.

4. A kinetic control of the reaction in the transition state was suggested in Ref. 69, since the reactions of trisubstituted DD'D" complexes with primary and secondary amines, as well as complexes of the DD'D' type with primary amines in donor solvent, yielded "regular" tetrasubstituted clathrochelates DD"D" or $DD_1"D_2"$. Accordingly, monosubstituted complexes of the $Bd_2D'$ type in donor solvents have interacted with primary amines to produce $C_2$-symmetric or $C_2$-nonsymmetric $Bd_2D"$ clathrochelates depending on the nature of amine. The secondary aliphatic amines in the donor solvents have interacted exclusively with complexes of the $Bd_2D'$ type formed by primary amines only.

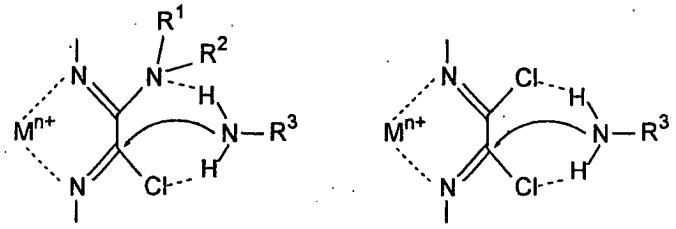
Thus, one can state that an inductive effect of the substituents is distributed uniformly throughout the whole macrobicyclic system, and, unlike the well-studied substitution in aromatic systems, there is no pronounced *ortho*, *para*, and *meta* effects of the substituents in clathrochelates. A key role in the transfer of electromeric interactions in a clathrochelate molecule is played by the encapsulated central metal ion, rather than a $\sigma, \pi$-bond system. Therefore, the electron interactions in the clathrochelate molecule are distributed isotropically rather than alternately [69].



As a result, thermodynamic control of the reactivity of a clathrochelate is affected by the sum of the partial effects of the substituents introduced, whereas kinetic control in the transition state is determined by steric factors, solvation, and orientation effects. Most unexpected proved to be a preferential orientation of the second amine substituent in the *vic*-position relative to the first introduced. This phenomenon is explained by the orientation effects of a hydrogen bond in the transition state (Scheme 25). The necessary transition state is facilitated by the occurrence of a hydrogen bond with the amino group involved. This determines the trend of the reaction *via* the route A. As for the use of solvents, hydrogen bond acceptors ($CHCl_3$ and $CH_2Cl_2/RNH_2^+Cl^-$) lead to a decrease in the nucleophilic properties of the solvated amine and hamper the orientation of the reacting species in the transition state. As a result, the reaction stops at an earlier stage: trisubstituted products in the case of hexachloride precursors and monoamine clathrochelates in the case of dichloride precursors are formed in the reaction with primary sterically unhindered aliphatic amines [69].

The synthesis of boron-capped clathrochelate iron(II) tris-dioximates has been realized for wide range of substituents at the boron atom. The attempts to obtain analogous trialkyl- and triaryl-tin-capped iron(II) compounds have not been successful. In the some cases, polymeric clathrochelate compounds have been formed, especially when reactions proceed under basic conditions. With tin(IV) iodide, the primarily formed soluble green complexes also readily transform into polymeric red compounds that are presumably associated with the detachment of iodide ions because of steric hindrance between substituents in dioxime fragments and the bulky iodide atoms of capping groups [70].

Attempts to use other tin halogenides (preferentially tin(IV) tetrachloride) as capping agents have turned out to be more




**Scheme 25**

successful. In the case of acyclic and alicyclic α-dioximates, tribromotin-capped complexes, like their trichlorotin-capped analogs, have also readily formed. Contrariwise, aromatic dioximes with bulky substituents as a phenyl or furyl radicals did not formed tribromotin-capped clathrochelates because of steric hindrances. In the case of $SnF_4$, reactions proceed with greater difficulties. A relatively high yield was obtained for the complex with nioxime, which has a *cis*-configuration that implies a higher stability of the resultant complex. As for acyclic dioximes, the reaction with $SnF_4$ in the presence of $Fe^{2+}$ ion was carried out only for dimethylglyoxime and methylglyoxime. Unlike the germanium-capped clathrochelates, the corresponding complexes with other acyclic α-dioximes have failed to arise by a remetallation reaction [70]. In particular, an attempt to employ the reaction between alkoxyboron-capped $FeBd_3(BOCH_3)_2$ complex and an excess of $SnF_4$ in ethanol for the preparation of the corresponding trifluorotin-capped macrobicyclic complex met with failure. It appears that the difficulties encountered in the formation of trifluorotin-capped complexes are accounted for by the rupture of a strong Sn–F bond and the detachment of the fluoride ion. Besides, the fluoride anion is capable of removing $SnF_4$ from the reaction, and it favours the occurrence of side reactions.

Unlike the synthesis of $(HAm)_2[FeD_3(SnCl_3)_2]$ compounds, the reactions carried out with $SnF_4$ and $SnBr_4$ require a prolonged refluxing at the first stage; otherwise, semiclathrochelate complexes might be formed. It was noted that when the initial iron(II) salt with a halogen different from that in tin(IV) tetrahalogenide was used, a mixture of products with various state of substitution of one halogenide ion by another in the capping group (as seen from $^{119}Sn$ NMR spectra) resulted [70].

$$Fe^{2+} + 3H_2D + 2SnCl_4 + 6DEA \longrightarrow (HDEA)_2\left[\text{Cl}_3\text{Sn}\text{–}D_3(Fe^{2+})\text{–}\text{SnCl}_3\right] + 2Cl^- + 4HDEA^+ \quad (16)$$

Diethylamine and tetra-*n*-butylammomium salts of the clathrochelate $[FeD_3(SnCl_3)_2]^{2-}$ dianion were obtained by template



condensation of a variety of acyclic, aromatic and alicyclic dioximes ($H_2Gm$, $H_2Mm$, $H_2Dm$, $H_2Bd$, $H_2Fd$, $H_2Nx$, $H_24MNx$ and $H_2Ox$) with tin(IV) tetrachloride on the $Fe^{2+}$ ion in *iso*-propanol [71] (Reaction 16).

The nioximate dianion was also isolated as a salt with a $HPy^+$ cation.

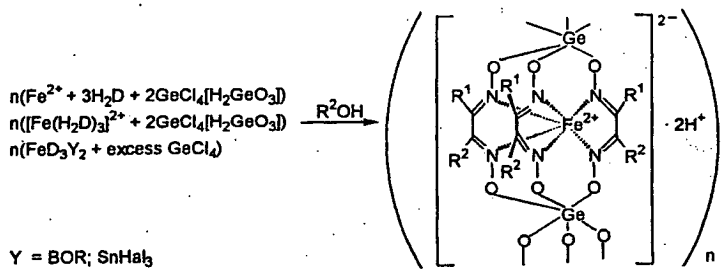
Clathrochelate $(HAm)_2[FeD_3(SnCl_3)_2]$ complexes were also formed by cross-linking of the initial nonmacrocyclic iron(II) tris-dioximates with tin(IV) tetrachloride either in acetone or in an acetone-benzene mixture with subsequent addition of amine [71]:

$$[Fe(H_2D)_3]^{2+} + 2SnCl_4 + 6Am \longrightarrow (HAm)_2[FeD_3(SnCl_3)_2] + 2Cl^- + 4HAm^+ \quad (17)$$

Direct Reaction 16 is likely to proceed *via* an intermediate step, i.e., the formation of a protonated tris-complex. Although the product yield of Reaction 17 is higher, Reaction 16 is preferred because of the difficulties encountered in the isolation of nonmacrocyclic iron(II) tris-dioximates. Tin-capped complexes also arise from the interaction of the Tchugaev type $Fe(HD)_2Am_2$ bis-dioximates with tin(IV) tetrachloride, and from the labile boron-capped $FeD_3(BOR)_2$ complexes with a great excess of $SnCl_4$.

The cross-linking of iron(II) tris-dioximates with germanium tetrachloride occurs *via* a somewhat unexpected pathway: instead of the expected formation of the clathrochelate $[FeD_3(GeCl_3)_2]^{2-}$ dianion, in the case of certain dioximes ($H_2Nx$, $H_2Dm$ and $H_2Mm$) the direct reaction in the alcohol medium yielded polymeric $[FeD_3(Ge_2O_3)\cdot xSolv]_n$ complexes. Deep red-coloured clathrochelate $[FeD_3(GeCl_3)_2]^{2-}$ dianions have been observed in both DMF and DMSO media. However, attempts to isolate monomeric $(HAm)_2[FeD_3(GeCl_3)_2]$ complexes from such solutions were not successful. In all cases, only polymeric compounds were obtained. The germanic acid, formed upon dissolution of $GeO_2$ in water, can also serve as the capping agent that favours the formation of such polymeric compounds. It appears that germanium(IV) alcoholates can also act as capping agents; however, the formation of monomeric compounds in this case is impossible since these alcoholates are apt to hydrolyze. The cross-linking of the nonmacrocyclic iron(II) tris-dioximates implemented for nioximate turned out to be more efficient than a direct template reaction [72].

A direct template synthesis has failed for α-benzyldioxime and glyoxime, for which germanium-capped clathrochelate complexes were prepared by remetallation (capping group exchange) reactions.




**Scheme 26**

In this case, a two-stage detachment of the capping groups of the initial clathrochelate complex presumably takes place with the simultaneous cyclization with another capping agent (Scheme 26).

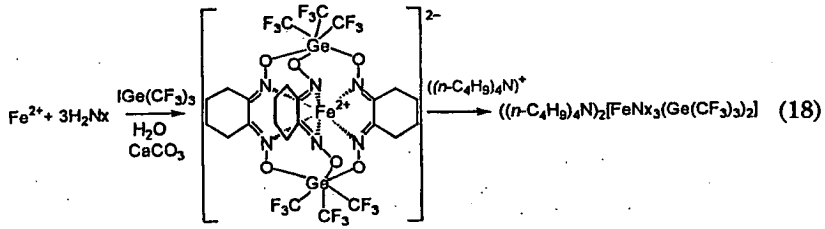
The high stability of the complexes formed in the acidic medium was emphasized. This stability may account for the formation of certain polymeric structure upon capping with germanium tetrachloride accompanied by the detachment of $H^+$ ions. The formation of polymeric clathrochelate compounds has also been observed when $(HAm)_2[FeD_3(SnHal_3)]$ compounds in water or $Fe^{2+}$-$H_2D$-$SnHal_2$ systems in methanol have been treated with strong bases (e.g., NaOH and $C_2H_5ONa$). In the second case, tin(II) ion has been oxidized by air oxygen to a tin(IV) ion that acts as the capping agent. However, in the case of tin-capped compounds, brightly colored clathrochelate complexes partly retain in the aqueous solution [1].

The use of electron-accepting perfluoroalkyl substituents instead of the electron-donating alkyl ones increases the Lewis acidity of the corresponding cross-linking agents. It was suggested that $IGe(CF_3)_3$ may be a promising capping agent in the synthesis of monomeric germanium(IV) compounds. Trifluoromethyl substituents form one of the two triangular bases of the resultant octahedral coordination polyhedron of the capping germanium atom and, since the Ge–C bond is inert in substitution reactions, impede the polymerization reactions, which are typical for germanium halides and alcoholates. Thus, the perfluoroalkyl groups have proved to be protecting and activating at the same time [73].

[1] The known analytical reaction for a qualitative determination of microamounts of iron with dioximes after reduction with tin(II) chloride responsible for the intense coloring of the solution is, in our opinion, caused by the formation of such clathrochelate complexes.

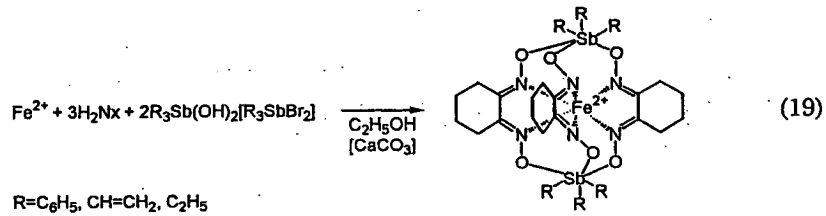


The first monomeric tris(trifluoromethyl)germanium-capped clathrochelate was prepared by template condensation of nioxime and $IGe(CF_3)_3$ on a $Fe^{2+}$ ion:




The nonmacrocyclic iron(II) tris-complex (an intermediate product in the synthesis of clathrochelates, see Chapter 4) have readily reacted with two molecules of $IGe(CF_3)_3$ in aqueous solution. In this case $IGe(CF_3)_3$ formed dianionic octahedral capping groups. The $H^+$ ions released in the course of the reaction were neutralized by calcium carbonate. The resultant clathrochelate $[FeNx_3(Ge(CF_3)_3)_2]^{2-}$ dianion was isolated as a salt with a bulky organic $(n\text{-}C_4H_9)_4N^+$ cation [73].

The synthesis of clathrochelates resulting from capping with antimony(V) compounds was realized for the first time as described in Ref. 74. With antimony(V) halogenides, only polymeric complexes were isolated, but antimony(V) triorganyles, unlike tin(IV) triorganyles, readily form nioximate iron(II) clathrochelates by Reaction 19.

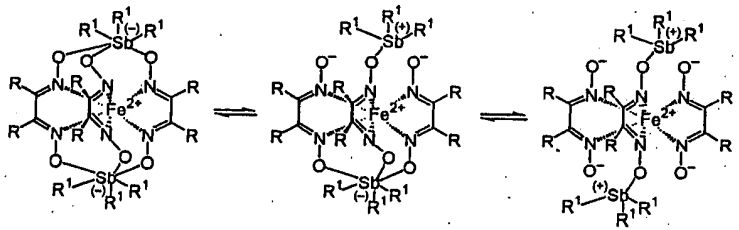



Reaction 19 was carried out in dry ethanol by the interaction of $FeCl_2 \cdot 4H_2O$ and nioxime with triphenylantimony(V) dihydroxide, and trivinylantimony and triethylantimony(V) dibromides. In the cases of dibromides, an excess of $CaCO_3$ was added [74].

As described above, the $C_2$-nonsymmetric boron- and boron-tin-capped clathrochelate compounds can be prepared by a solid-phase synthesis on the element oxide surface that serves as both a matrix

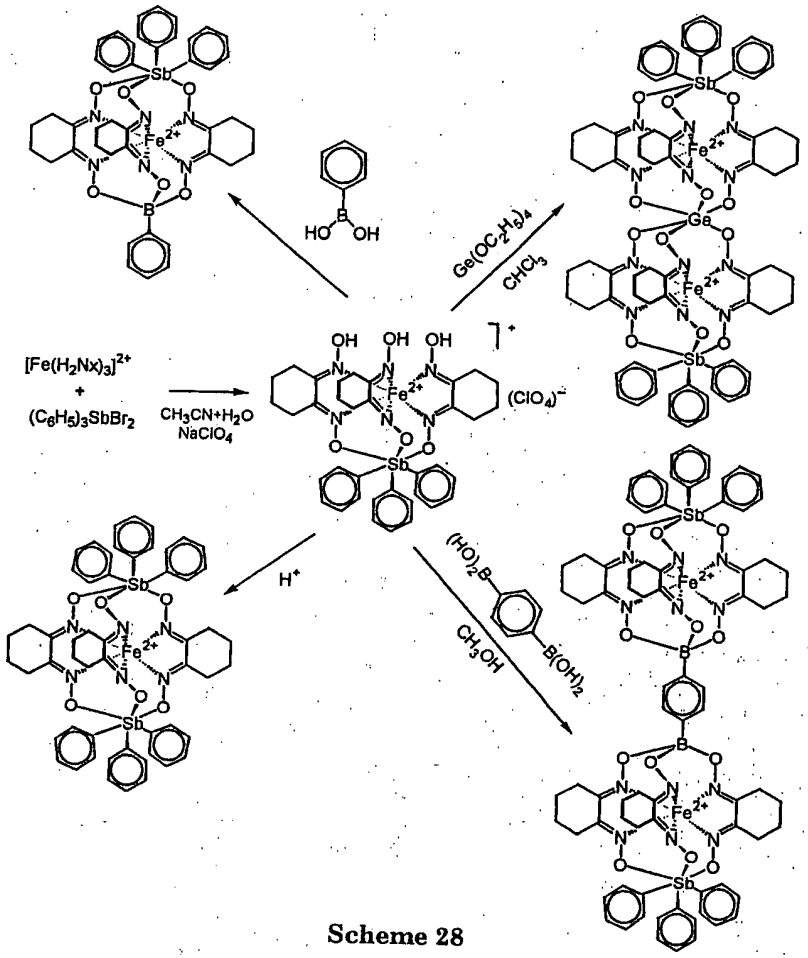
and a topochemical protecting group. At the same time, such a synthetic route is rather complicated, and it may be applied to only a limited number of compounds. Alternative methods for directed synthesis of $C_2$-nonsymmetric clathrochelates and polyclathrochelates from the preliminarily prepared semiclathrochelates and modification reactions of the apical capping fragments were proposed in Ref. 75. The lability of antimony-capped iron(II) semiclathrochelates and clathrochelates and the fact that one (targeted) complex can be isolated from several possible products in the course of reaction have determinated a successful synthesis of $C_2$-nonsymmetric mono- and bis-clathrochelates. Antimony-capped complexes proved to be far more labile than their boron- and tin-capped analogs, for which a remetallation (a capping group exchange) reaction has first been observed [70]. The chemical behaviour of such antimony-capped complexes occupied an intermediate position between that of the clathrochelate and that of molecular adducts, and a considerable "onic" contribution to their geometry cannot be excluded (Scheme 27).

The determination of the conditions under which the $[Fe(HNx)_3(Sb(C_6H_5)_3)](ClO_4)$ semiclathrochelate forms and can be isolated seems to be very important, since semiclathrochelate tris-dioximates except this one have readily undergone disproportionation (see Scheme 9) to yield more kinetically and thermodynamically stable clathrochelates. Even in the case of a triethylantimony derivatives with similar geometry and properties, the simultaneous occurrence of capping and disproportionation reactions could not be avoided, and, therefore, the $[Fe(HNx)_3(Sb(C_6H_5)_3)](ClO_4)$ complex proved to be the first tris-dioximate semiclathrochelate that was isolated and characterized [75]. The reaction of the $[Fe(HNx)_3(Sb(C_6H_5)_3)](ClO_4)$ semiclathrochelate with mono- and bifunctional capping agents (Lewis acids) other than $(C_6H_5)_3Sb(OH)_2$



Scheme 27






Scheme 28

and its derivatives led to the formation of $C_2$-nonsymmetric mono- and bis-clathrochelates (Scheme 28).

The clathrochelates with a labile triethylantimony capping group have undergone remetallation in the presence of silicon dioxide as a catalyst. The reaction did not occur under mild conditions in the absence of $SiO_2$, and under hard conditions it yielded a mixture of

products. The first stage leads to the formation of a surface-immobilized antimony-silicon-capped clathrochelate, which is desorbed from the surface with another capping agent to give a $C_2$-nonsymmetric mono- or bis-clathrochelate depending on the nature of this agent (Scheme 29).

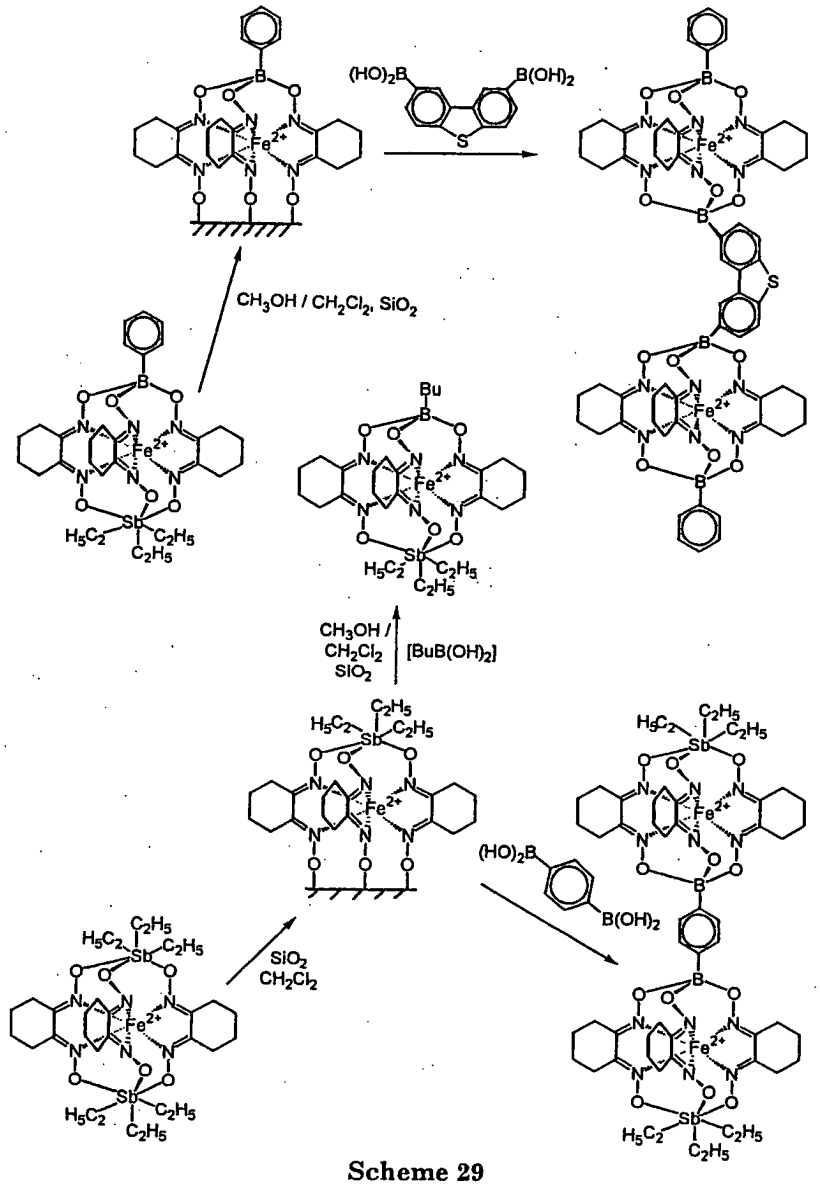
The fact that antimony-containing Lewis acids, unlike boron-containing cross-linking agent, are apt to form semiclathrochelate (lacunar) complexes permits one to obtain a great variety of $C_2$-nonsymmetric mono- and polyclathrochelates and to employ them as syntones. An appreciable change in the stability to capping group dissociation in the series $Sb_2$-cap << SbB-cap << $B_2$-cap complexes allows one to employ them for the directed synthesis of polynuclear boron-capped complexes with stepwise preparation of chainlike clathrochelates (Scheme 30), the triorganylantimony capping groups of which can be regarded as protecting groups [75].

For the first time, a macrobicyclic ruthenium (II) tris-dioximate was obtained by refluxing of $RuCl_3 \cdot 3H_2O$ and nioxime in dry ethanol under argon with subsequent cooling to room temperature and treatment with phenylboronic acid [76].

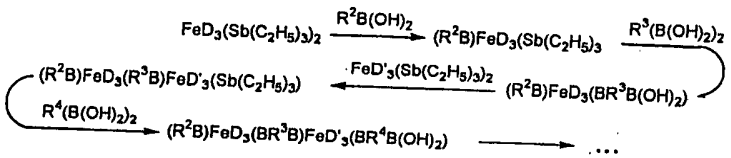
Ruthenium(II) clathrochelates have also been synthesized *via* interaction of $RuDMSO_4Cl_2$ solvato-complex and nioxime, α-benzyldioxime, and dimethylglyoxime with different boron-containing capping agents in THF. The use of this solvato-complex as an initial ruthenium(II) salt substantially increases the yield of clathrochelates. For instance, in the preparation of $RuNx_3(BC_6H_5)_2$, the use of $RuDMSO_4Cl_2$ solvato-complex instead of $RuCl_3 \cdot 3H_2O$ salt enhances the yield from 12.5 to 45%. The majority of macrobicyclic ruthenium(II) $RuNx_3(BR)_2$ tris-dioximates (where R is F, $CH_3$, $C_6H_5$, *n*-$C_4H_9$, $OCH_3$, $OC_2H_5$, O*n*-$C_3H_7$, *iso*-$C_3H_7$, O*n*-$C_4H_9$, O*n*-$C_5H_{11}$ and O*n*-$C_{10}H_{21}$) were obtained in high yields with nioxime. Acyclic dioximate $RuBd_3(Bn\text{-}C_4H_9)_2$, $RuBd_3(BOCH_3)_2$, $RuDm_3(Bn\text{-}C_4H_{10})_2$, and $RuDm_3(BOCH_3)_2$ clathrochelates were isolated in much lower yields [77].

A keen recent interest in polyimine ruthenium(II) complexes (tris-bipyridinates, tris-phenanthrolinates, and their analogues) has largely been evoked by the ample scope they offer as selective DNA-cleaving agents and probes in biochemistry. Such ruthenium(II) complexes, as well as their photophysics, are of particular interest in creating the devices for molecular electronics (e.g., systems of the "light-switch" type) and in analytical detection of metal ions as well.






**Scheme 29**




**Scheme 30**

In the majority of research performed, the chelating ligands have preliminarily been functionalized, and this has permitted one to obtain ruthenium(II) complexes with improved chemical and physicochemical properties. Through a highly conjugated aromatic system, both the medium (solvent and acidity) and functionalizing substituents influence the energy of the central metal ion *d* orbitals and ligand $\pi,\pi^*$-orbitals. An electronic effect of aliphatic and aromatic substituents in the dioximate fragments in the series of the above described boron-capped ruthenium(II) clathrochelates is substantially lower. Such substituents exhibit low reactivity, and their modification with variations in physicochemical parameters (and, consequently, in the corresponding characteristics of the clathrochelates itself) is rather complicated. The several procedures for the synthesis of ribbed-functionalized macrobicyclic ruthenium(II) complexes starting from the reactive chloride clathrochelates were proposed in Ref. 78.

Several pathways for the synthesis of ribbed-functionalized tris-dioximate clathrochelate complexes (i.e., clathrochelates with functionalizing substituents in α-dioximate fragments) have been thoroughly analyzed above. The optimal synthetic route is based on a preliminary isolation of a reactive halogenide precursor and its further functionalization *via* nucleophilic substitution reactions so well known in organic chemistry. The syntheses of ruthenium(II) clathrochelates are complicated by a kinetic inertness of the initial ruthenium solvato-complexes in the reactions of coordinated ligand substitution, as well as by the ability of ruthenium complexes to form intra- and intermolecular redox reactions, frequently with participation of coordinated ligands. Moreover, the $Ru^{3+}$ ion is apt to form stable square-planar bis-dioximates. Therefore, an attempt to extend the procedures of the precursor synthesis, described above for iron(II), to ruthenium(II) ion without any modification met with failure. The poor donor ability displayed by the dichloroglyoxime does not permit one to obtain clathrochelate ruthenium(II) precursors



starting from $RuDMSO_4Cl_2$ solvato-complex in the manner described above for boron-capped ruthenium(II) clathrochelates with aromatic, alicyclic, and acyclic dioximes. The syntheses of hexachloride ruthenium(II) precursors were realized under hard conditions (in particular, a mixture of nitromethane and $SbCl_3$, or boiling TFA, or boiling $BF_3{\cdot}O(C_2H_5)_2$ were used as a reaction media) with much lower yields compared with reactions with iron(II) ion [78].

The approach employed was highly successful because of the low basicity and high protolytic stability of the dichloroglyoxime. In most cases, the $Ru^{2+}$ ion generated *in situ* during the reduction of oxychloride ruthenium compounds in the higher oxidation states with metallic lead in the presence of electron-accepting $SbCl_3$-type ligands also favored the elimination of chloride ions from the inner coordination sphere of ruthenium ions. As a result, the $Ru(Cl2Cm)_3(BF)_2$ and $Ru(Cl2Gm)_3(Bn\text{-}C_4H_9)_2$ precursors were obtained with reasonable yields. However, the hard conditions required for the activation of the $Ru^{2+}$ ions in the reaction with poorly coordinating dichloroglyoxime impose restrictions on the use of the previously proposed synthetic routes. Such methods can be employed only when capping agents (in particular, $BF_3$, alkylboronic acids, and their derivatives) are stable to protolytic dissociation. When arylboronic acids and their derivatives (especially phenylboronic acid), which are more apt to protolytic dissociation and transmetallation, were employed as capping agents, one could observe an abrupt decrease in the desired product yield induced by the destruction of the capping agent. Thus, the reaction involved two competitive processes: the formation of a clathrochelate, which precipitates from the reaction mixture because of its low solubility (this shift the equilibrium in the desired direction), and a protolytic dissociation of the capping agent. Consequently, one should determine the optimal conditions for a synthetic procedure (time and temperature) that make it possible on the one hand to achieve a maximal formation of the desired complex, and one the another hand to avoid a significant decomposition of the capping agent, which can eventually lead to the decomposition of the already-formed complex. To avoid such negative phenomena during the synthesis, the capping agent must be added periodically in excess [78].

The reactivity of hexachloride ruthenium(II) precursors in the reactions of nucleophilic substitution is somewhat lower than that of their analogs with an encapsulated iron(II) ion. The hexathiophenol

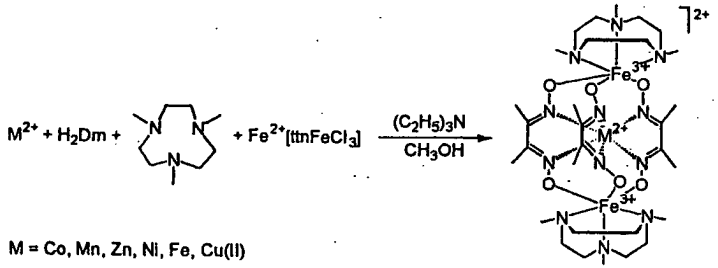
clathrochelate was obtained when potassium thiophenolate (not the $C_6H_5SH/K_2CO_3$ system) was used.

The reaction of $Ru(Cl2Gm)_3(BC_6H_5)_2$ precursor with a 15% excess of *n*-butylamine (calculated from a tetrasubstituted clathrochelate) in DMF at 0°C for 2 h resulted solely in trisubstituted clathrochelate, and the substitution took place in two of the three dioximate fragments. (Scheme 31). To produce tetrasubstituted product, a twofold excess of *n*-butylamine was used, and the reaction mixture was stirred for 10 h at room temperature. An unexpected result was obtained when DMF was replaced by chloroform: the interaction of $Ru(Cl2Gm)_3(BC_6H_5)_2$ with *n*-butylamine both at room temperature and with a prolonged stirring at 50÷60°C yielded only one trisubstituted product [78].

As with iron(II) complexes, the di- and tricrown ether ruthenium(II) clathrochelates were isolated depending on the molar ratio precursor/salt of (bis-(2-(*o*-oxyphenoxy))diethyl ether and on the reaction time [78].

Drago and Elias's idea [46] to employ tridentate amines for protection of one of the two triangular bases of hexacoordinate *d*-metal ions coordination polyhedron (in case the latter act as capping agents) from polymerization has successfully been developed by P. Chaudhuri and K. Wieghardt for the synthesis of linear homo- and heterotrinuclear macrobicyclic complexes with tris-dioximate bridging ligands.

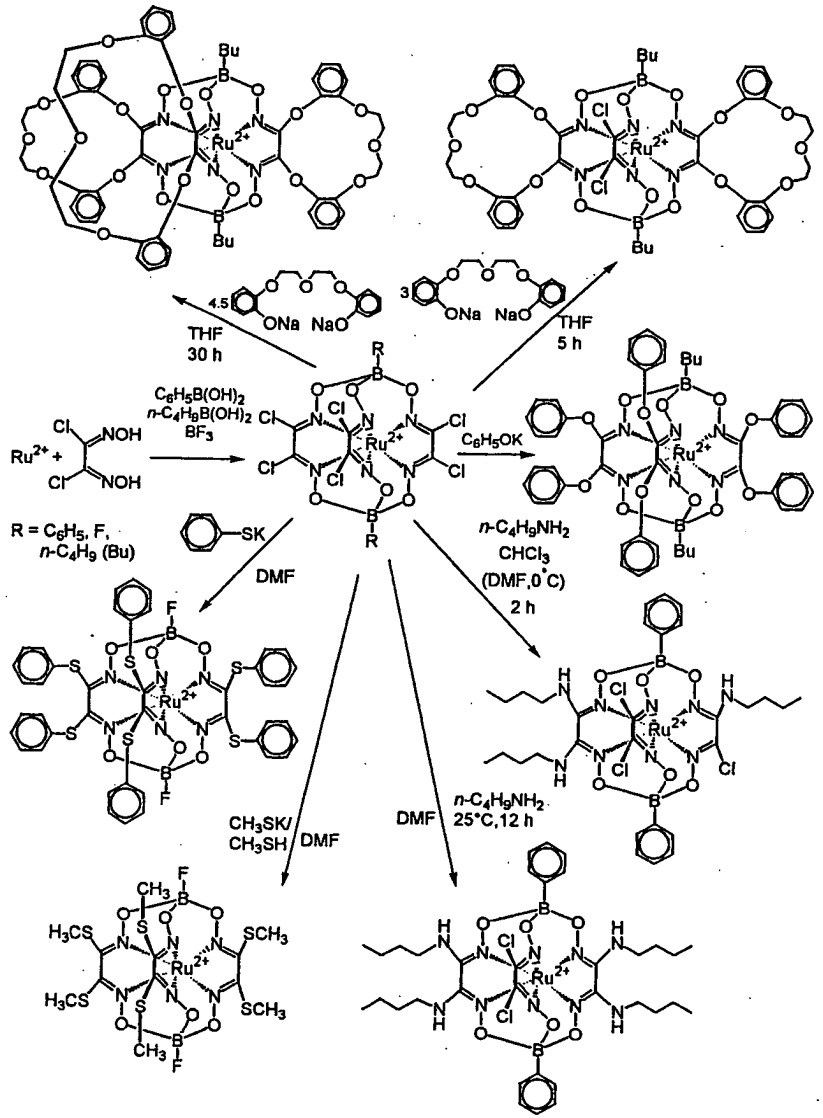
The first $[M^{II}Dm_3(ttnFe)_2](ClO_4)_2$ complexes of this type were obtained [79] by the interaction of iron(II) acetate and copper, zinc, nickel, cobalt, and manganese acetates with dimethylglyoxime and 1,4,7-trimethyl-1,4,7-triazacyclononane (*ttn*) in methanol in the presence of triethylamine (Reaction 20). In this case, a triazamacrocycle served as the protecting group in the octahedral capping $ttnFe^{III}O_3$ fragment.




(20)

M = Co, Mn, Zn, Ni, Fe, Cu(II)

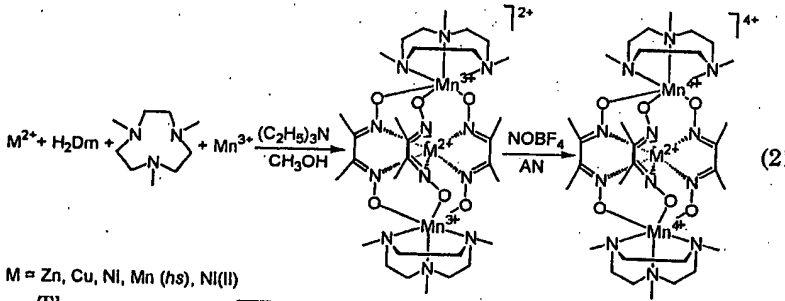





**Scheme 31**

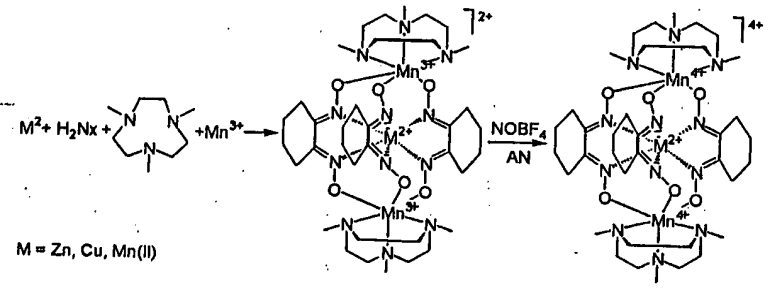
The template synthesis with $ttnFe^{3+}$ cation as capping agent (Reaction 20) has also made it possible to isolate the clathrochelate nickel(II) $[NiDm_3(ttnFe)_2](ClO_4)_2$ and $[NiDm_3(ttnFe)_2](PF_6)_2 \cdot 0.5CH_3OH$ tris-dioximates arising from the interaction of either $Fe^{3+}$ ions, *ttn*, and nonmacrocyclic nickel(II) tris-dimethylglyoximate (formed under basic conditions with the action of triethylamine), or $Ni^{2+}$ ions and dimethylglyoxime in the presence of $ttnFeCl_3$ complex in methanol [80].

Manganese-capped $[M^{II}Dm_3(ttnMn^{III})_2](ClO_4)_2$ tris-dimethylglyoximates were first synthesized [81] by an analogous procedure (Reaction 21). The oxidation of manganese-containing capping groups with nitrosyl ions led the formation of the $[M^{II}Dm_3(ttnMn^{IV})_2](ClO_4)_2$ clathrochelates with a capping manganese(IV) atoms. The synthetic procedures for these complexes were described more thoroughly in Ref. 82.




(21)

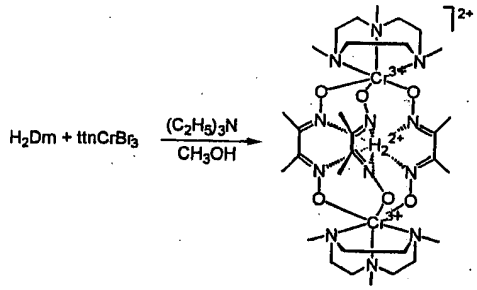
The manganese(III)-capped tris-nioximate macrobicycles, also oxidized to manganese(IV)-capped clathrochelates, were obtained in higher yields [83]:




(22)



An attempt to use $Cr^{3+}$ ions as capping agents produced unexpected results. The prolonged refluxing of $ttnCrBr_3$ complex, dimethylglyoxime, and triethylamine in methanol resulted in first doubly protonated free macrobicyclic $[H_2Dm_3(ttnCr^{III})_2](ClO_4)_2$ ligand *via* Reaction 23 [84].




(23)

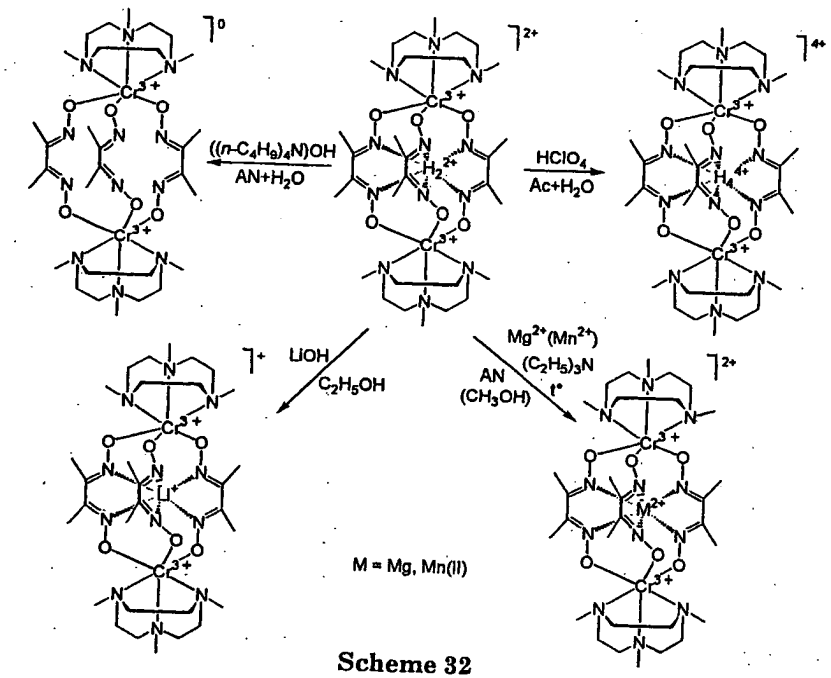
This free clathrochelate ligand has been employed for the synthesis of nonprotonated and tetraprotonated free cages using tetra-*n*-butylammonium hydroxide and $HClO_4$, respectively, as well as chromium(III)-capped magnesium, manganese(II) and lithium clathrochelates (Scheme 32) [85].

Chromium(III)-capped clathrochelate complexes were also obtained by a direct reaction in the presence of $Cu^{2+}$, $Ni^{2+}$, $Fe^{2+}$ and $Co^{2+}$ ions (Scheme 33). In the latter case the central ion underwent oxidation in the course of the reaction, and a cobalt(III) clathrochelates was isolated.

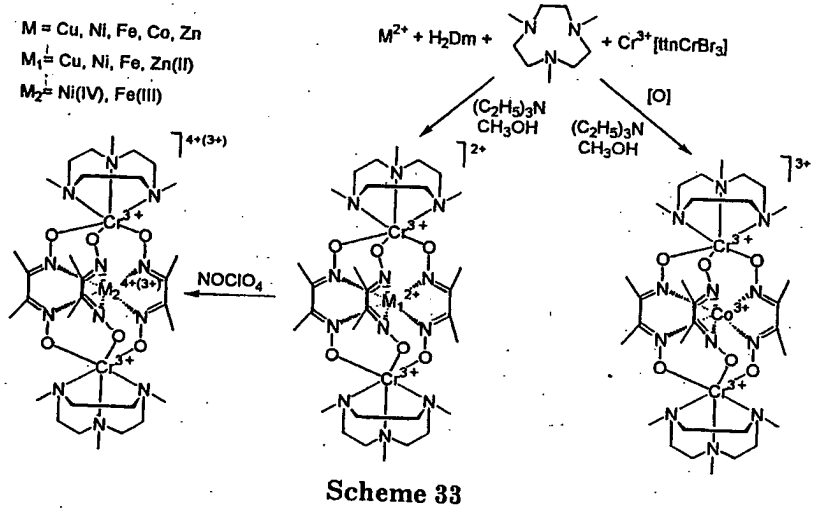
An analogous zinc-containing clathrochelate resulted from capping with an initial $ttnCrBr_3$ compex [86]. The encapsulated nickel and iron(II) ions were oxidized with nitrosyl perchlorate to nickel(IV) and iron(III) ions in acetonitrile (Scheme 33) [85].

Attempts to isolate clathrochelate technetium(III) tris-dioximates *via* template cross-linking three dioxime molecules with alkylboronic acid have not been successful. Only semiclathrochelate $TcNx(HNx)_2(BR^2)Hal$ and $TcDm(HDm)_2(BR^2)Hal$ complexes (where $Hal^-$ is $Cl^-$, $Br^-$; $R^2$ is $CH_3$ and $n$-$C_4H_9$) were prepared [87, 88].

The tin-capped $^{99}Tc(HDm)_2(H_2Dm)(\mu\text{–}OH)(SnCl_3)$ and $^{99}Tc(HNx)_2(H_2Nx)(\mu\text{–}OH)(SnCl_3)$ complexes were obtained by the reduction of $NH_4TcO_4$ with $SnCl_2$ in the presence of α-dioxime in aqueous/alcohol HCl solution (Scheme 34) [89, 90].

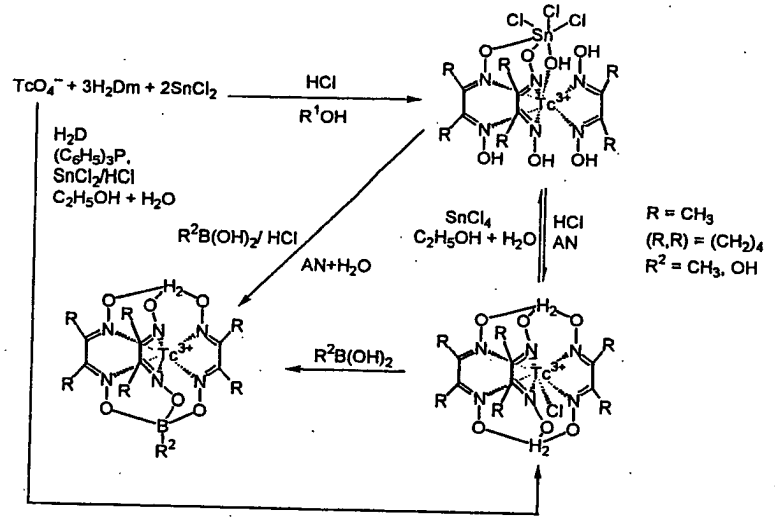



**Scheme 32**




**Scheme 33**






**Scheme 34**

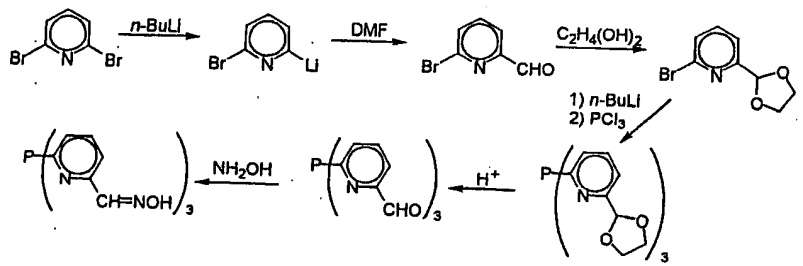
The addition of HCl to a solution of the complexes obtained caused the formation of non-capped $Tc(H_2Dm)(HDm)_2Cl$ and $Tc(H_2Nx)(HNx)_2Cl$ compounds. These compounds have reacted with $SnCl_4$ to reform the initial tin-capped complexes.

Both non-capped and tin-capped products were cross-linked with an excess of the boric and methylboronic acids to form the corresponding semiclathrochelate $[TcD(HD)_2(BR^2)]^+$ cations [89, 90].

## 2.2 SYNTHESIS OF MACROBICYCLIC PHOSPHORUS-CONTAINING *d*-METAL TRIS-DIIMINATES

Clathrochelates of this type were synthesized starting from semiclathrochelate phosphorus-containing tris-diimine ligand, which was obtained by Scheme 35.

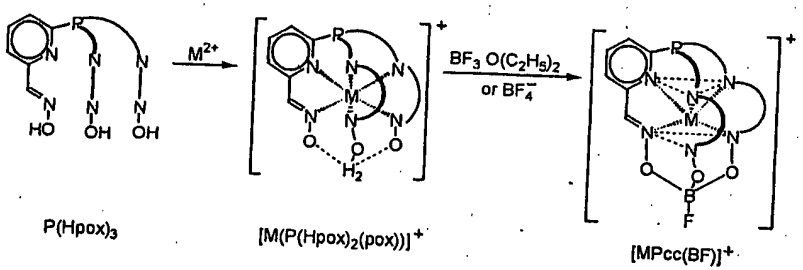
The resultant ligand readily formed semiclathrochelate $[M(P(Hpox)_2(pox))]^+$ complexes (where M is nickel, copper, cobalt, or zinc(II) ions) by the interaction of metal salts, e.g., perchlorates, with *P(Hpox)*$_3$ ligand either in dry ethanol or in acetonitrile. Attempts to isolate analogous iron(II) and manganese(II) complexes gave no desired results [91, 92]. Direct synthesis of the macrobicyclic




**Scheme 35**

complexes (without the isolation of semiclathrochelate products) was realized *via* interaction between a tetrafluoroborate $M(BF_4)_2 \cdot 6H_2O$ salt (where M is iron, cobalt, nickel, and zinc(II) ions) and *P(Hpox)*$_3$ ligand in acetonitrile followed by capping with boron trifluoride etherate [92]. [CoPcc(BF)]$(BF_4)$ and [NiPcc(BF)]$(BF_4)$ complexes were also synthesized by capping of the semiclathrochelate [Ni(P(Hpox)$_2$(pox))]$(ClO_4)$ and [Co(P(Hpox)$_2$(pox))]$(ClO_4)$ compounds with $BF_3 \cdot O(C_2H_5)_2$. This is evidence in favour of the synthesis of macrobicyclic complexes occurring through the formation of a semiclathrochelate compound intermediate step (Scheme 36).

In an attempt to isolate the [M(P(Hpox)$_2$(pox))] $(BF_4)$ complexes, it was revealed [92] that the $BF_4^-$ anion cross-linked a semiclathrochelate complex yielding the corresponding [MPcc(BF)]$(BF_4)$ clathrochelates. This made it possible to synthesize [MPcc(BF)]$(BF_4)$ complexes by an alternative pathway using $NaBF_4$ as a capping agent. Boiling of the corresponding salt $M(BF_4)_2 \cdot 6H_2O$, *P(Hpox)*$_3$ ligand, and $NaBF_4$ in acetonitrile for several hours followed by treatment with water yielded complexes identical to those obtained by the above procedure [92].




**Scheme 36**



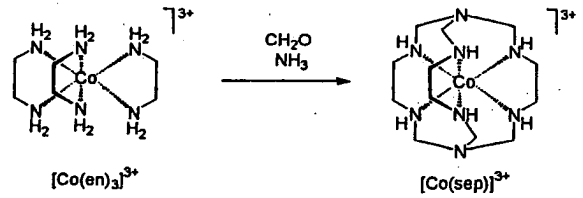
A similar reaction pathway was also employed to prepare the nickel(II) complex with a macrobicyclic *4-MePcc(BF)* ligand [93]. Attempts to obtained macrobicyclic manganese(II) and copper(II) complexes of this type from the corresponding semiclathrochelate complexes have not been successful [92].

## 2.3 SYNTHESIS OF SEPULCHRATES AND SARCOPHAGINATES

A template synthesis of macrobicyclic ligand is, as in the cases considered, also most important pathway for the preparation of sepulchrates and sarcophaginates. However, modification reactions of free ligands and complexes, as well as synthesis from the free ligands (preformed by template condensation on the metal ion followed by demetallation or synthesized by other methods) are of particular importance in the preparation of these types of clathrochelates. The specific features observed in the synthesis of sepulchrates and sarcophaginates are accounted for by the fact that their structural peculiarities distinguishes them from other clathrochelates. First, these ligands have a specific flexibility that allows the synthesis of complexes with metal ions of a different nature and in various oxidation states, as well as allowing the free ligands to be obtained by demetallation of preformed clathrochelate complexes. Second, a considerable number of stereoisomers that fairly readily convert to each other can be obtained. Numerous reactive sites provide a wide range of modification reactions of ligands and complexes for the preparation of sepulchrates and sarcophaginates. These complexes seem also to be obtained by metal ion substitution.

Sepulchrates and sarcophaginates have primarily been synthesized *via* template macrocyclization of the preformed metal tris-diaminates with capping agents, which is regarded as being the most significant approach to the synthesis of these compounds. Sargeson and coworkers first prepared the cobalt(III), platinum(IV), and rhodium(III) sepulchrates and sarcophaginates as well as the corresponding cobalt(II) complexes [94, 95].

The [Co(sep)]$Cl_3$ complex is obtained from Reaction 24 between cobalt(III) [Co(en)$_3$]$Cl_3$ tris-ethylenediaminate and dilute aqueous solutions of ammonia and formaldehyde in the presence of lithium carbonate with subsequent isolation of the product by IEC [94-96]:

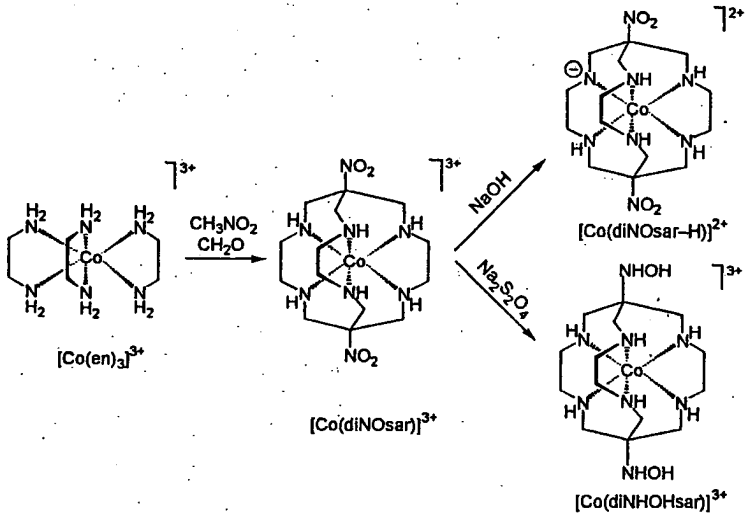



(24)

Several variants of the first-developed procedure have been reported [97-100].

The corresponding macrobicyclic cobalt(II) $[Co(sep)](ZnCl_4)\cdot H_2O$ complex was prepared by reduction of the $[Co(sep)]Cl_3$ complex with zinc dust in aqueous HCl [95]. A similar procedure was used for the synthesis of the dithionate $[Co(sep)](S_2O_6)$ salt in the presence of $Li_2S_2O_6$ [99]. The optically active *R*- and *S*-isomers of cobalt sepulchrate were obtained from the optically active parent Δ-$[Co(en)_3]Cl_3$ and Λ-$[Co(en)_3]Cl_3$ complexes [94-95].

The use of nitromethane instead of ammonia has resulted in the formation of the $[Co(diNOsar)]Cl_3\cdot H_2O$ sarcophaginate [94, 101].




(25)

A similar procedure was employed to obtain the $[Co(diNOsar)]^{3+}$ cation optically active isomers and salts of other anions [101]. A more rational approach to the synthesis of this clathrochelate was reported in Ref. 102.



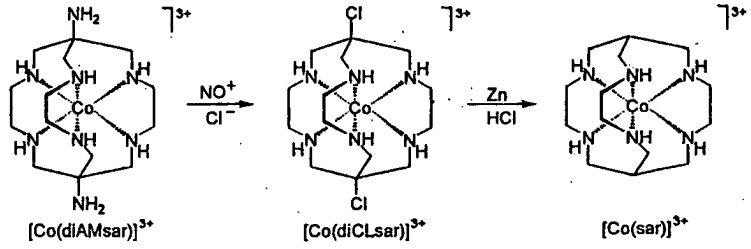
Monoimine, N-methylated, and semiclathrochelate complexes have been isolated and identified as by-products of sarcophaginate synthesis to gain a deeper insight into the reaction mechanism. The addition of sodium hydroxide to an aqueous solution of $[Co(diNOsar)](ClO_4)_3$ complex leads to a change in the colour of the solution from orange to violet. The violet crystals of the deprotonated $[Co(diNOsar–H)](ClO_4)_2$ compound were isolated [101].

Partial reduction of $[Co(diNOsar)]Cl_3\cdot H_2O$ complex with $Na_2S_2O_4$ in slightly acidic medium yielded a sarcophaginate containing hydroxylamine groups in apical fragments [103]. This complex was also prepared using organic radicals as reductant [104].

The $[Co(diNOsar)](ClO_4)_3$ sarcophaginate easily reduces with zinc dust in neutral aqueous solution to the corresponding cobalt(II) compound. To avoid the reduction of the nitro groups, the reaction must proceed quickly. The resulting $[Co(diNOsar)](ClO_4)_2$ complex is unstable and on storage decomposes because of intramolecular redox processes [94, 101].

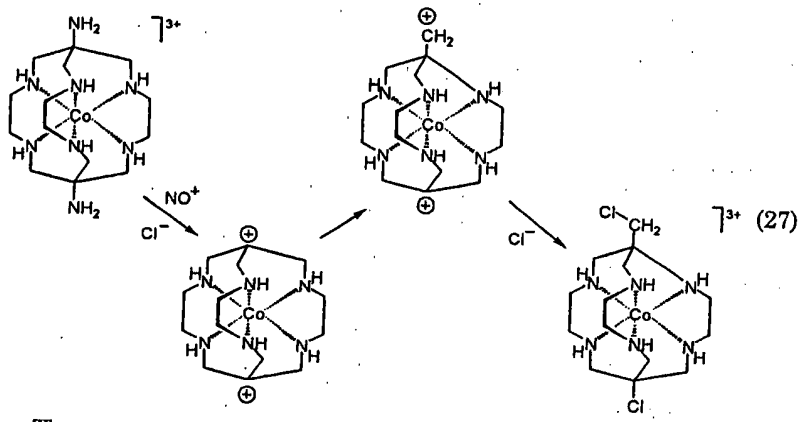
The reaction of the $[Co(diNOsar)]^{3+}$ cation with zinc dust in acidic medium has proceeded to the reduction of nitro groups to amino groups, which are protonated and, therefore, not affected by treatment with hydrogen peroxide. As a result, the $[Co(diAMsar)]Cl_3\cdot 2HCl$ and $[Co(diAMHsar)]Cl_5$ diaminosarcophaginates were isolated, which makes it possible to synthesize sarcophaginates with different substituents in the capping group [101]. It was also observed that cobalt(II) and cobalt(III) aminosarcophaginates resulted from a catalytic hydrogenation of cobalt(III) dinitrosarcophaginate [105].

Nitrosation of $[Co(diAMsar)]^{3+}$ cation in the presence of chloride anion led to the formation of cobalt dichlorosarcophaginate, the reduction of which with zinc dust and subsequent treatment with $H_2O_2$ and HCl gave the simplest $[Co(sar)]Cl_3$ sarcophaginate [94, 101]:




(26)

An intermediate $[Co(CLsar)]Cl_3$ monochlorosarcophaginate has also been formed. In addition to clathrochelate $[Co(diCLsar)]^{3+}$ cation, nine compounds were isolated from two main fractions ("orange" and "yellow") of the nitrosation products by IEC [101]. The first one contained unreacted $[Co(diNOsar)]Cl_3$ (3%), $[Co(CLNOsar)]Cl_3$ (18%), $[Co(HONOsar)]Cl_3$ (7.5%), $[Co(HOCLsar)]Cl_3$ (26%), $[Co(diHOsar)]Cl_3$ (1.5%) and the expected $[Co(diCLsar)]Cl_3$ (44%) sarcophaginates. The second fraction was a mixture of complexes of a contracted *absar* ligand that arose from intramolecular rearrangement:




(27)

The contracted $[Co((ClME)CLabsar)]Cl_3$ (60%), $[Co((ClME)NOabsar)]Cl_3$ (20%), $[Co((ClME)HOabsar)]Cl_3$ (17%), and $[Co(AMH(ClME)absar)]Cl_4$ (3%) sarcophaginates were isolated from the "yellow" fraction by IEC.

Thus, apart from the expected $[Co(diCLsar)]Cl_3$ complex, the nitrosation of $[Co(diAMsar)]^{3+}$ diaminosarcophaginate yielded four regular sarcophaginates and four contracted *absar* ligand complexes [101].

The rearrangement mechanism of a cobalt(III) nitrosarcophaginate in the basic conditions to yield a contracted $N_6$-cage, as well as the intermediate reaction products are described in Ref. 106 (see Chapter 4).

The hydrolytic stability of the $[Co(diCLsar)]^{3+}$ cation toward conversion to the $[Co(diHOsar)]^{3+}$ dihydroxysarcophaginate is due to the difficulty of forming a carbocation at a planar bridgehead position. It was noted that the nitrosation of $[Co(diAMsar)]^{3+}$ sarcophaginate occurring without rearrangement involves competition of all nucleophiles in solution, whereas its nitrosation with rearrangement appears to involve chlorine anion selectively [101].



The ethylenediaminate fragments of the sarcophaginate frameworks exhibit certain flexibility, which enables them to have conformations from the λ (the Δ-$C_3lel_3$ form) to δ (the Δ-$D_3ob_3$ form). Conformations *"lel"* and *"ob"* define the parallel and oblique orientation of the C–C bond of the ethylenediaminate moiety relative to the $C_3$ axis, respectively. The existence of intermediate forms as energetically stable conformations is also possible [107]. Theoretical interpretation of the $Co^{2+/3+}$ electron transfer and electrochemical and chiroptical properties is hampered by the need to consider several accessible conformations of the cobalt(II) and cobalt(III) sarcophaginates and sepulchrates.

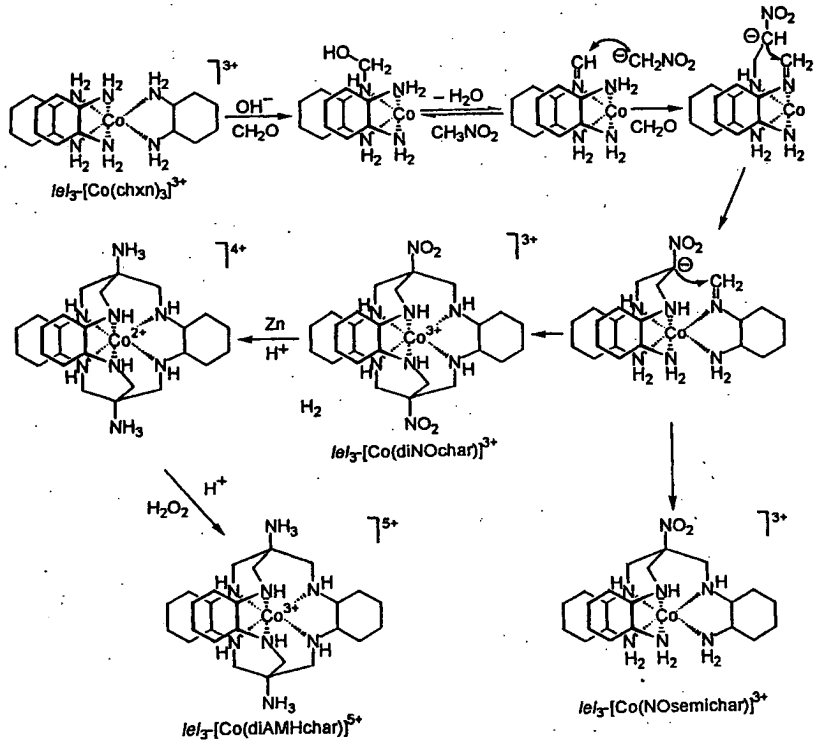
Application of the template encapsulation procedure to the rigid cyclohexanediaminate *lel*$_3$-$[Co(chxn)_3]^{3+}$ cation has yielded a high symmetric cage systems [107]. For the synthesis of the diaminocyclohexane sarcophaginates, the condensation procedure was modified (pH 11÷12 and elevated temperatures) compared with that for ethylenediamine sarcophaginates.

The resolved (+)-(*S,S*)- and (–)-(*R,R*)-*trans*-1,2-cyclohexanediamine isomers reacted with a cobalt(II) salt in methanol upon air bubbling to yield Λ-*lel*$_3$-$[Co(chxn)_3]Cl_3 \cdot 4H_2O$ and Δ-*lel*$_3$-$[Co(chxn)_3]Cl_3 \cdot 4H_2O$ tris-diaminates, respectively. Capping of these tris-complexes in aqueous solution at pH 11.5 with a great excess of nitromethane and formaldehyde upon heating to 55°C gave Λ-*lel*$_3$-$[Co(diNOchar)]Cl_3 \cdot 3H_2O$ and Δ-*lel*$_3$-$[Co(diNOchar)]Cl_3 \cdot 3H_2O$ sarcophaginates in 50% yield. Nitromethane (16-fold excess) and formaldehyde (10-fold excess) were added in portions, and readjustment of the solution to pH 11.5 was periodically carried out. The products obtained were isolated by IEC [107]. Only *lel*$_3$-$[Co(NOsemichar)]Cl_3 \cdot 5H_2O$ semiclathrochelate has been formed at room temperature.

Reduction of the Δ-*lel*$_3$-$[Co(diNOsar)]Cl_3 \cdot 3H_2O$ sarcophaginate with zinc dust followed by treatment with concentrated aqueous $NaClO_4$ yielded the cobalt(II) Δ-*lel*$_3$-$[Co(diNOchar)](ClO_4)_2 \cdot 2H_2O$ clathrochelate. The Δ- and Λ-*lel*$_3$-$[Co(diAMHchar)]Cl_5 \cdot 6H_2O$ diamino-sarcophaginates were obtained by reduction of the reaction mixture with zinc dust in aqueous HCl after template encapsulation at 50°C without isolation of the dinitrosarcophaginates (Scheme 37). At room temperature, reduction of these dinitrosarcophaginates gave the $[Co(AMHNOchar)]Cl_4 \cdot 6H_2O$ semiproduct. Reduction of the

cobalt(III) Δ-*lel*$_3$- diaminosarcophaginate with zinc dust and subsequent treatment of the reaction mixture with $Li_2ZnCl_4$ resulted in the cobalt(II) Δ-*lel*$_3$-[Co(diAMchar)]$(ZnCl_4)\cdot 2H_2O$ sarcophaginate (Scheme 37) [107].

The clathrochelate cyclohexanediamine complexes display a high chemical stability. For instance, heating a cyclohexanediamine cobalt (III) sarcophaginate in 5 molar NaOH at 200°C and a cobalt(II) sarcophaginate in a sealed ampule with concentrated hydrochloric acid at 270°C for 24 h leads to only slight decomposition of the complex. No change from the *lel* sarcophaginate isomer to its *ob* form was observed. Attempts to cross-link the preformed *ob*$_3$-[Co(chxn)$_3$]$^{3+}$ cation resulting in the *ob*$_3$-[Co(diNOsar)]$^{3+}$ sarcophaginate have also failed. However, the *ob* and *lel* forms of such complexes were

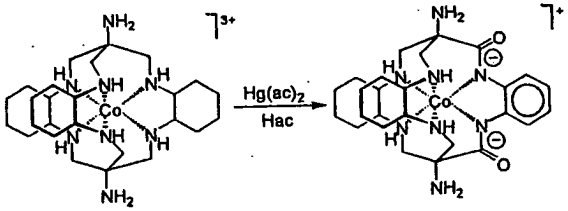



**Scheme 37**



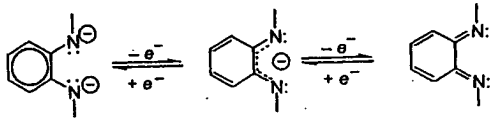
synthesized by capping the meridional (*mer*-) and facial (*fac*-) *lel*$_3$-[Co(1,2pn)$_3$]$^{3+}$ cation isomers. The $Co^{3+}$ ion was then removed from the chiral cage and recoordinated. Under these conditions a small quantities of the *ob* isomer were obtained and separated from the *lel* form by IEC [5].

Several novel clathrochelate complexes have also been prepared *via* the oxidation of preformed sarcophaginates. The cyclohexane-diamine fragments of *char* sarcophaginate underwent oxidation with mercury(II) acetate in acetic acid to give the diamide complex (Reaction 28). In addition, one of the cyclohexane rings has also been aromatized:




(28)

The resultant sarcophaginate may be oxidized by a two-electron mechanism to the *o*-benzoquinonediimine derivative. Reduction of the latter by a three-electron mechanism carried the cage complex back to an aromatic cobalt(II) derivative:



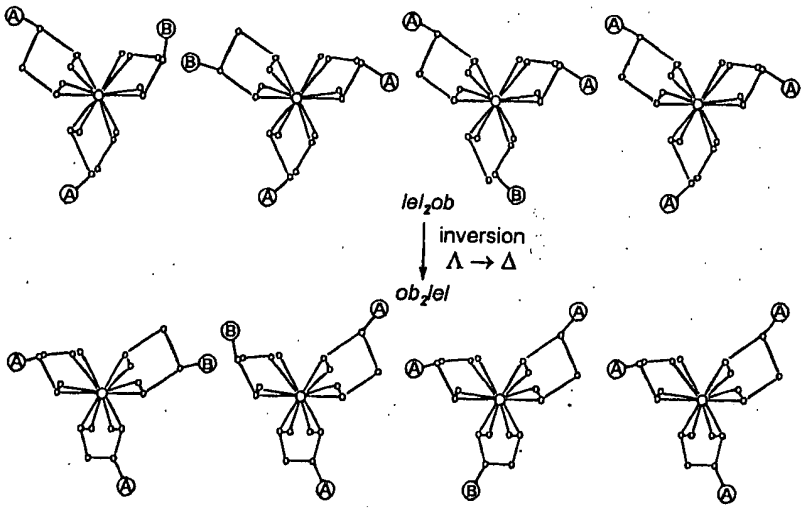

(29)

Cerium(III) or tin(II) ions were chosen as a reductant [5]. Application of redox processes is promising for the synthesis of novel sarcophaginates with higher stability and a small cavity size. The reactivity of sarcophaginate ligands may also be employed to prepare imine-, hydroxylamine-, and amide-containing systems not only with cyclohexanediamine derivatives, but with simpler clathrochelates as well.

A mixture of [Co(diNOl,2pnsar)]$^{3+}$ diastereoisomers was obtained by capping of [Co(*R*,*S*-1,2pn)$_3$]$^{3+}$ tris-diaminate (containing *lel*$_3$ (36%), *lel*$_2$*ob* (42%), *ob*$_2$*lel* (18%), and *ob*$_3$ (4%) conformers) with formaldehyde and nitromethane under basic conditions followed by reduction with zinc dust in aqueous HCl. The resultant mixture was

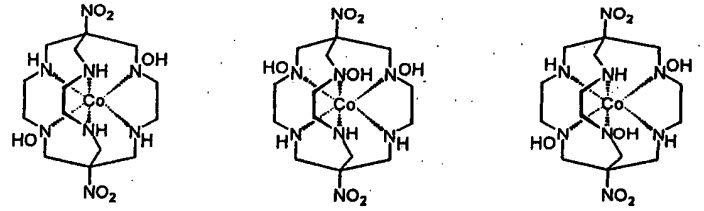
separated by IEC. Alongside *fac-* and *mer-* isomers of the *lel*$_3$-[Co(diAMl,2pnsar)]$^{3+}$ complex (in 23% yield), four products were recovered and identified as one *fac* and three *mer* isomers of the *lel*$_2$*ob* conformers of this sarcophaginate (the total yield is *ca* 11%). The *ob*$_2$*lel* and *ob*$_3$ isomers were prepared in a similar manner, i.e. by demetallation of three *lel*$_2$*ob*-[Co(diAMl,2pnsar)]$^{2+}$ isomers with concentrated NaCN aqueous solution and subsequent interaction between the resultant free clathrochelate ligands and *trans*-[CoPy$_4$Cl$_2$]Cl complex in 2-methoxyethanol. In this case *ca* 10% of the (*S*$_2$,*R*)-*lel*$_2$*ob* cage has been inverted to the (*S*$_2$,*R*)-*ob*$_2$*lel* conformer (Scheme 38) [5].

Reaction of the [Co(diCLsar)]$^{3+}$ cation with hydrogen peroxide under basic conditions yielded the monohydroxylamine [Co(diCLsar·NOH)]$^{3+}$ complex even with an excess of the oxidant. The hydroxylamine group is stable toward strong oxidants ($Cr_2O_7^{2-}$, $Ce^{4+}$) but is reduced with zinc powder as well as $Cr^{2+}$, $Eu^{2+}$, and $V^{2+}$ ions to a secondary amine [5, 108]. Only one of the six coordinated secondary amino groups of the cobalt dichlorosarcophaginate is oxidized to the hydroxylamine group, whereas in the case of cobalt dinitrosarcophaginate, two or three of groups undergo such oxidation because the first complex exhibits higher basicity ($pK_a$ = 10.36) than the second ($pK_a$ = 9.87). In the majority of




Scheme 38





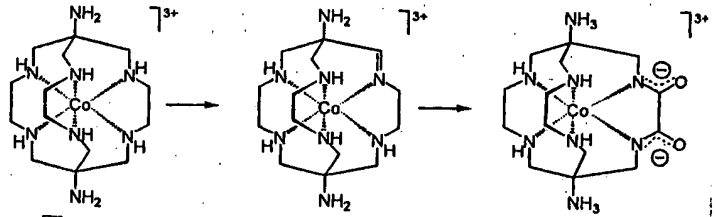

Scheme 39

cases, coordinated amino groups are too basic ($pK_a$ = 14) to deprotonate readily in aqueous solutions. As a consequence, they cannot be attacked by electrophilic $H_2O_2$ and oxidized [108].

Addition of hydrogen peroxide and base in equimolar amount to the [Co(diNOsar)]$^{3+}$ cation aqueous solution led to the formation of a monohydroxylamine [Co(diNOsar·NOH)]Cl$_3$·3H$_2$O complex. The treatment of the [Co(diNOsar)]$^{3+}$ cation with a large excess of $H_2O_2$ and base gave the product mixture. Three different complexes were isolated by IEC: a dihydroxylaminosarcophaginate **A** and trihydroxylaminosarcophaginates **B** and **C** (Scheme 39).

These complexes are less stable than the initial sarcophaginates, and their stability decreases in basic conditions. The hydroxylamine groups in these compounds demonstrated no reducing ability because the macrobicyclic ligand stabilises itself. Their further oxidation caused destruction of the clathrochelate framework [108].

Cobalt(II) sarcophaginates were oxidized to imines and amides. In the presence of activated carbon, oxygen, and cobalt(II) ions at pH 8.5, the [Co(diAMsar)]$^{3+}$ cation was oxidized first to imine and then through carbinolamine and amide to diamide sarcophaginate:



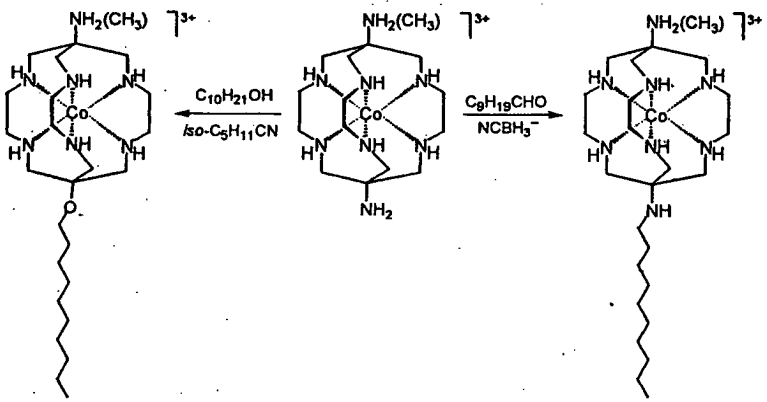
(30)

The same type of oxidation was also realized by mercury(II) acetate in acetic acid [5].

The relatively low nucleophilicity of the apical amino substituent in cobalt(III) diaminosarcophaginate has been used in acylation and alkylation reactions leading to a variety of apical functionalized cobalt(III) sarcophaginates with apical pendant aromatic and heteroaromatic substituents [109].

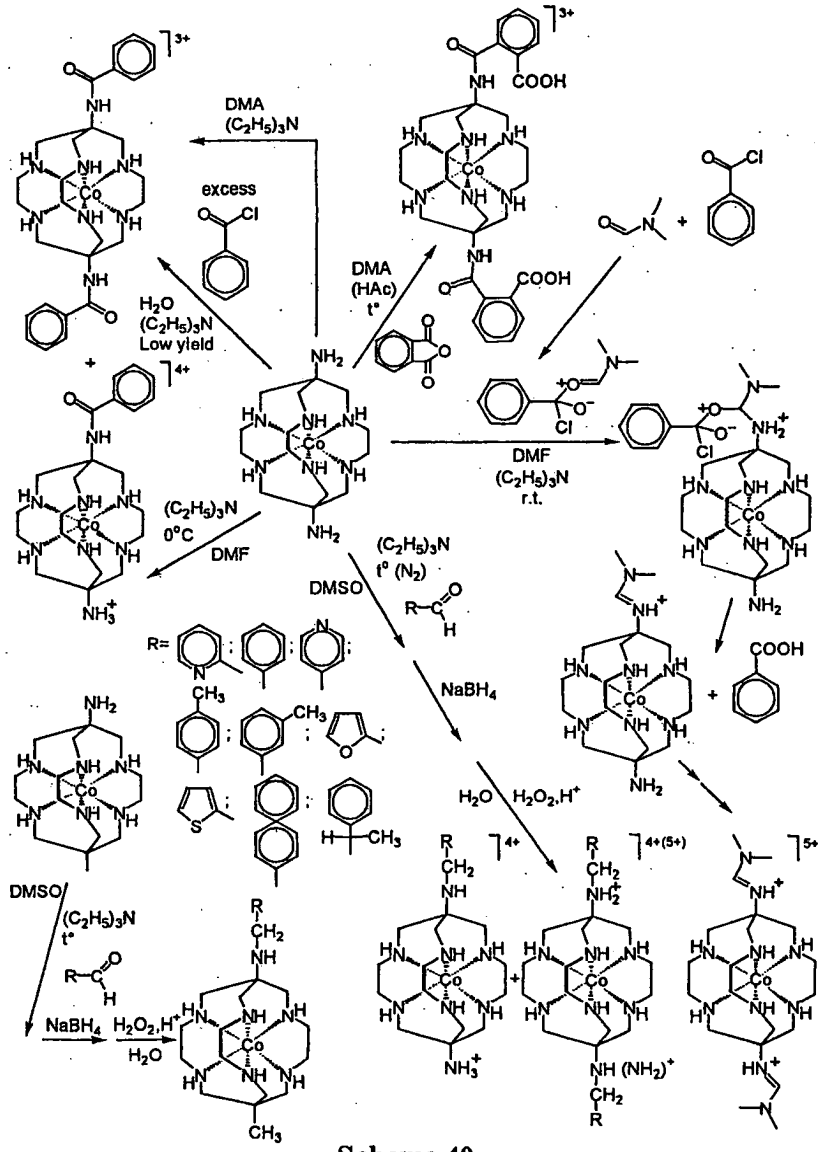
Attempts to react $[Co(diAMsar)]^{3+}$ cation with benzoyl chloride in aqueous solution resulted in mono- and dibenzoylated sarcophaginates in very low yields, and this reaction in other solvents such as AN, DMSO, and Py was even less successful, except in the cases of dimethylacetamide (DMA) and DMF. In last case, the benzoylated products along with formamidino-appended sarcophaginates were obtained in moderate yields by varying the reaction conditions (Scheme 40). The phthaloylation of cobalt(III) diaminosarcophaginates in both glacial acetic acid and DMA led to the formation of bis(phthalamic acid) derivative. The reductive alkylation of the $[Co(diAMsar)]^{3+}$ and $[Co(AMMEsar)]^{3+}$ cations with aromatic carbaldehydes resulted in mono- and 1,8-difunctionalized products (Scheme 40) in acceptable yields. As in the case of macrobicyclic tris-dioximates, the apical substitution of a sarcophaginate does not significantly modify the properties of the cage unit, and, correspondingly, the properties of the pendant groups do not appear to be substantially modified by the presence of the nearly clathrochelate cationic centre [109].

The reactivity of apical amino groups has been used in the synthesis of surface-active sarcophaginates (surfactants) [110]:



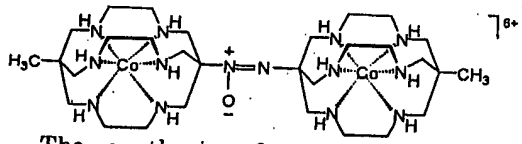

(31)






**Scheme 40**

Oxidation of the $[Co(MEAMsar)]^{3+}$ cation apical amino groups resulted in the bis-sarcophaginate:

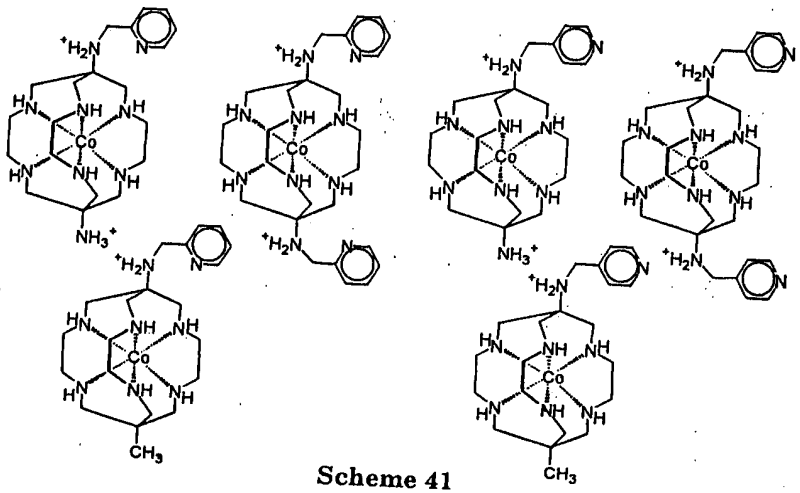


(32)

The synthesis of the cobalt cage complex with pendant pyridylmethyl arms (Scheme 41) was performed in excellent yield [111].

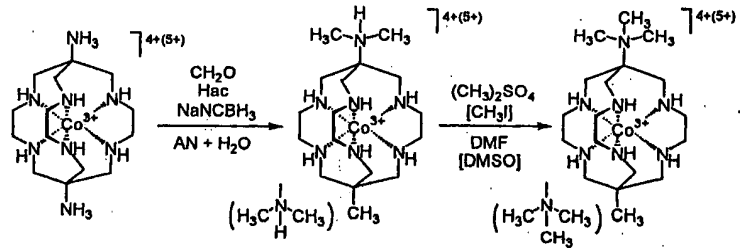
It is undoubtedly of interest that the substituents in the clathrochelate framework and in apical groups affect the structure and properties of macrobicyclic complexes. In particular, it was noted that N-methylation of the complexes must stabilize the lowest oxidation states of the encapsulated metal ion. In this case, one should take into account the steric effects of substituents whose introduction influences the dissociation kinetics of the sarcophaginates [112].

The copper and nickel(II) complexes of penta-, hexa-, and hepta-N-methylated sarcophaginate ligands showed tetradentate coordination of the metal ions, unlike the hexadentate coordination in regular sarcophaginates [113-115]. Exhaustive methylation of free *sar* ligand produced the highly lipophilic, hexatertiary base hexamethyl-sarcophagine [115].



**Scheme 41**

Stepwise methylation of apical amino substituents in cobalt(III) sarcophaginate make it possible to obtained a tris-N-methylated complex with conformational inversions in the ethylenediamine moieties from mainly a *lel*$_3$-conformation in $[Co(diAMsar)]^{3+}$ cation to an *ob*$_3$ conformation in $[Co(diMe_3AMHsar)]^{3+}$ sarcophaginate both in the solid state and in solution [116].

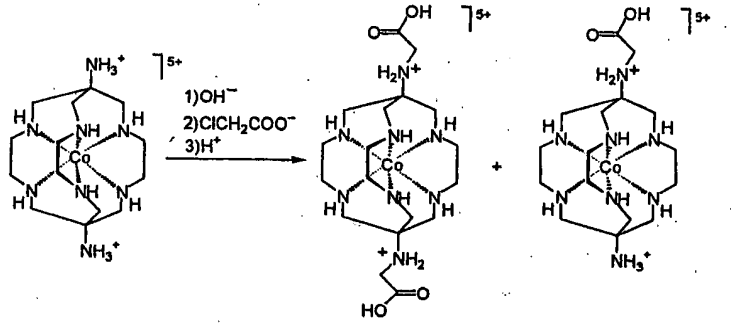


(33)

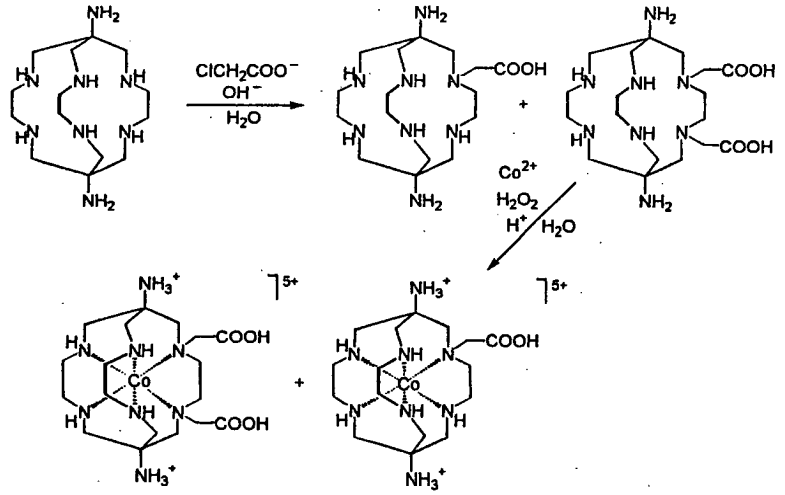
Free sarcophagines and their complexes were also modified by N-carboxymethylation with chloroacetate controlled by an encapsulated metal ion.

The reaction of a free diaminosarcophagine with an excess of chloroacetate under basic conditions led to a mixture of mono- and dicarboxymethylsarcophagines with substitution at the secondary nitrogen atoms; these were isolated as complexes with a cobalt(III) ion (Scheme 42) [117].

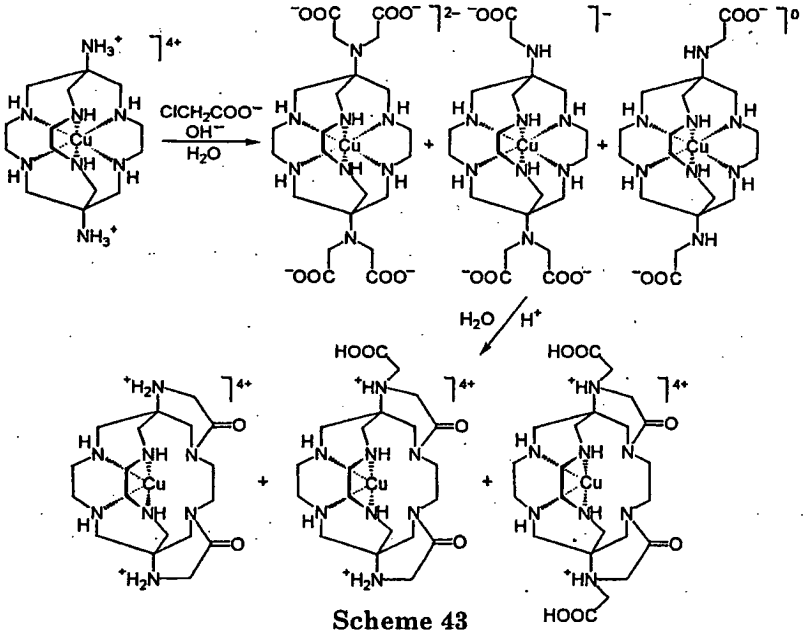
In the case of cobalt(III) diaminosarcophaginate, the Reaction 34 proceeded by an alternative pathway: only primary amino groups were involved to form apical mono- and difunctionalized sarcophaginates (in the latter case, only the symmetric product was obtained).



(34)



Scheme 42

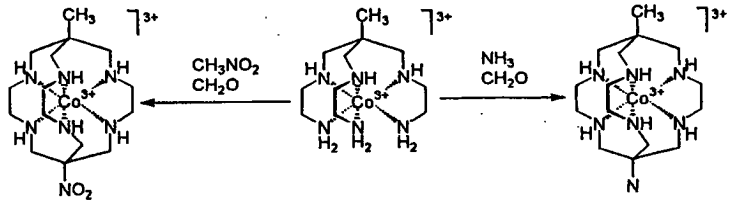


Scheme 43



The reaction of a copper(II) diaminosarcophaginate with chloroacetate made it possible to isolate complexes containing up to four functionalizing substituents in the apical fragment that undergo an intramolecular condensation to give lactam units in neutral and acidic media. The condensation involves one of the three ethylenediaminate fragments, and the copper(II) ion assumes a square-planar coordination (Scheme 43). A higher degree of carboxymethylation in the case of the copper(II) sarcophaginate was accounted for by the lower charge of the latter compared with that of a cobalt(III) complex. This caused a lesser reduction of the nucleophilicity of the uncoordinated primary nitrogen atoms [117].

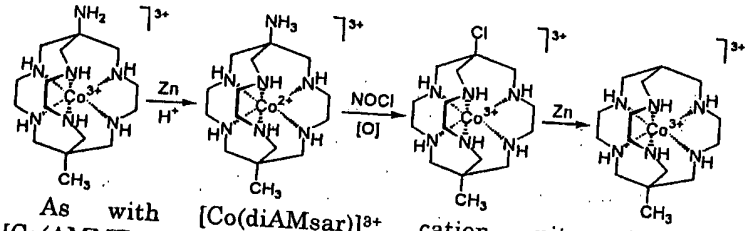
The use of the preformed semiclathrochelate ligands, first proposed in Ref. 94, is an alternative (and supplementary) approach to the synthesis of the sarcophaginates and sepulchrates. A semiclathrochelate *sen* ligand was employed to obtain sarcophaginates by template reaction of the $[Co(sen)]Cl_3$ complex with formaldehyde and ammonia to yield the $[Co(MEazasar)]Cl_3$ clathrochelate. A $[Co(N\text{-}sen)]Cl_3 \cdot 2H_2O$ complex was isolated as a by-product [96]. The resolution of $[Co(MEazasar)]^{3+}$ cation into its *S*- and *R*-isomers was achieved by IEC (aqueous sodium-antimony (+)-tartrate was used as an eluent). (+)-Co[(MEazasar)]$Cl_3$ sarcophaginate resulted from the (+)-$[Co(sen)]Cl_3$ semiclathrochelate as the initial compound [94]:



(35)

The reduction of $[Co(MEazasar)]Cl_3$ complex with a large excess of zinc dust in aqueous solution followed by treatment with hydrochloric acid and a $Li_2ZnCl_4$ solution yielded the cobalt(II) $[Co(MEazasar)](ZnCl_4) \cdot H_2O$ sarcophaginate [96].

Cross-linking of $[Co(sen)]Cl_3$ semisarcophaginate with nitromethane and formaldehyde led to the formation of the $[Co(NOMEsar)]Cl_3$ complex readily reducible to $[Co(AMMEsar)]Cl_3$ sarcophaginate. A detailed procedure for the preparation of $[Co(NOMEsar)]Cl_3$ complex was reported in Refs. 101 and 118. Nitrosation of $[Co(AMMEsar)]Cl_3$ clathrochelate accompanied by reduction with zinc dust resulted in the $[Co(MEsar)]Cl_3$ complex [94]:

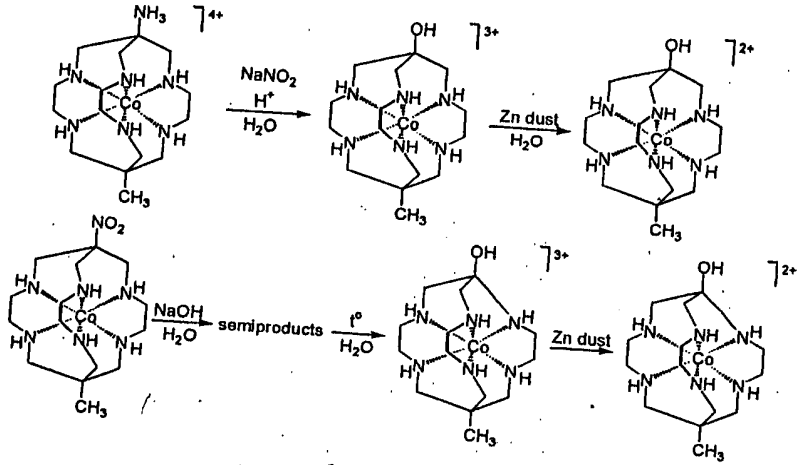



(36)

As with $[Co(diAMsar)]^{3+}$ cation, nitrosation of the $[Co(AMMEsar)]^{3+}$ cation led to the formation of "orange" and "yellow" fractions separated by IEC. The orange fraction contained the products of nucleophilic addition to carbanion without rearrangement (expected $[Co(ClMEsar)]Cl_3$ (*ca* 70%) and $[Co(HOMEsar)]Cl_3$ (*ca* 20%)sarcophaginates). The yellow fraction contained the product of nucleophilic addition to carbocation with rearrangement – $[Co((ClME)MEabsar)]Cl_3$ clathrochelate (*ca* 10%) [101].

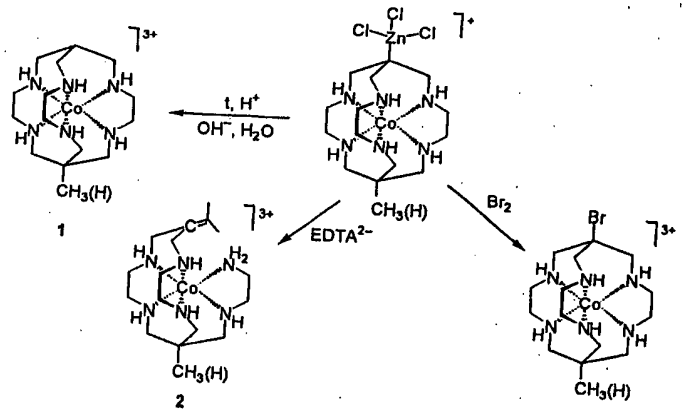
The isolation of both regular and contracted cobalt(III) $[Co(MEOHsar)]Cl_3$ and $[Co(MEOHabsar)]Cl_3$ hydroxysarcophaginates, as well as their analogs with an encapsulated cobalt(II) ion, obtained by reduction with zinc dust (Scheme 44), is described in Ref. 106.

The synthesis of $[Co(NOazasar)]^{3+}$ sarcophaginate was realized by two pathways starting from $[Co(NOsen)]^{3+}$ and $[Co(azasen)]^{3+}$ semiclathrochelates [119].




**Scheme 44**





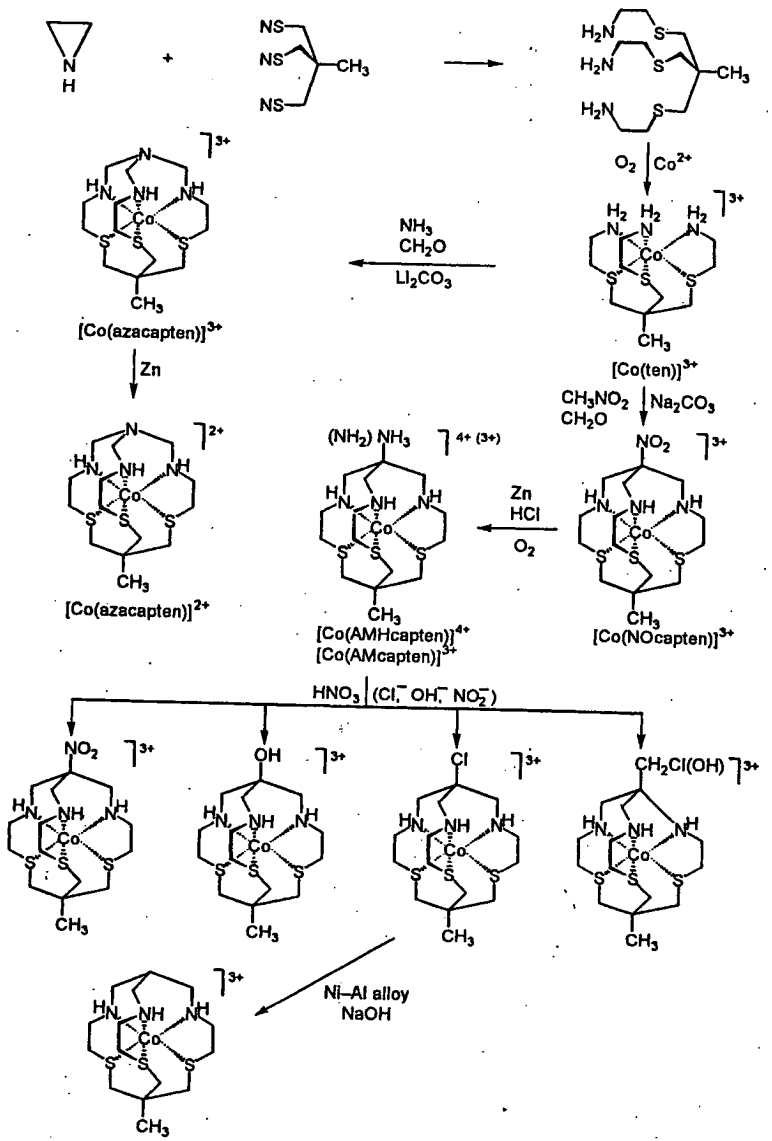

**Scheme 45**

During the synthesis of the methyne-capped cobalt(II) sarcophaginate *via* reduction of the chlorosarcophaginate complex with zinc dust in water (Scheme 45), an alkylzinc clathrochelate stable even in 6 molar hydrochloric acid was isolated [120].

Prolonged heating of the alkylzinc complex in acidic, neutral, or basic media resulted in the clathrochelate **1**. In the presence of $Na_2EDTA$, the rate of Zn–C bond cleavage is significantly faster because zinc ion forms a very stable complex with $EDTA^{2-}$ dianion. In addition to the initial sarcophaginate, olefin **2** was isolated. A bridgehead carbanion formed by the loss of zinc(II) ion can either capture a proton from the solvent (or any other additional electrophilic species including halogens, complex **3**) or rearrange to the olefin [120]. The unusual stability of the alkylzinc sarcophaginates also implies the possibility to synthesize relatively stable analogous magnesium, cadmium, aluminium, titanium, copper, cobalt, and nickel alkyl complexes [120].

The use of a semiclathrochelate hexadentate ligand is promising for the synthesis of sarcophaginates with different donor atoms, e.g. for the synthesis of $N_3S_3$-complexes. The $N_3S_3$–semisarcophaginate ligands were preliminarily synthesized in a high yield by refluxing 1,1,1-tris(mercaptomethyl)ethane and cyclohexane-1,3,5-trithiol with ethylene imine (Scheme 46) [121, 122].

The preformed semiclathrochelate $[Co(ten)]Cl_2(ClO_4)\cdot H_2O$ complex was capped with ammonia and formaldehyde in the presence of




**Scheme 46**



lithium carbonate to give a $[Co(azacapten)](ClO_4)_3 \cdot 2H_2O$ sarcophaginate, separated by IEC. The aqueous ammonium (+)-tartarate resolved the entantiomeric forms of this clathrochelate. The entantiomeric forms of the $[Co(ten)]Cl_2(ClO_4) \cdot H_2O$ complex were separated by the same technique.

Capping of $[Co(ten)]^{3+}$ cation with nitromethane and formaldehyde in aqueous solution in the presence of sodium carbonate gave the $[Co(NOcapten)]Cl_2(ClO_4) \cdot 3/2H_2O$ complex. The reduction of the latter with zinc dust in aqueous HCl followed by treatment with hydrogen peroxide yielded a $[Co(AMcapten)]Cl_3 \cdot 5/2H_2O$ sarcophaginate. Cobalt(II) compounds were readily obtained by reduction of the corresponding cobalt(III) complexes with amalgamated zinc [121].

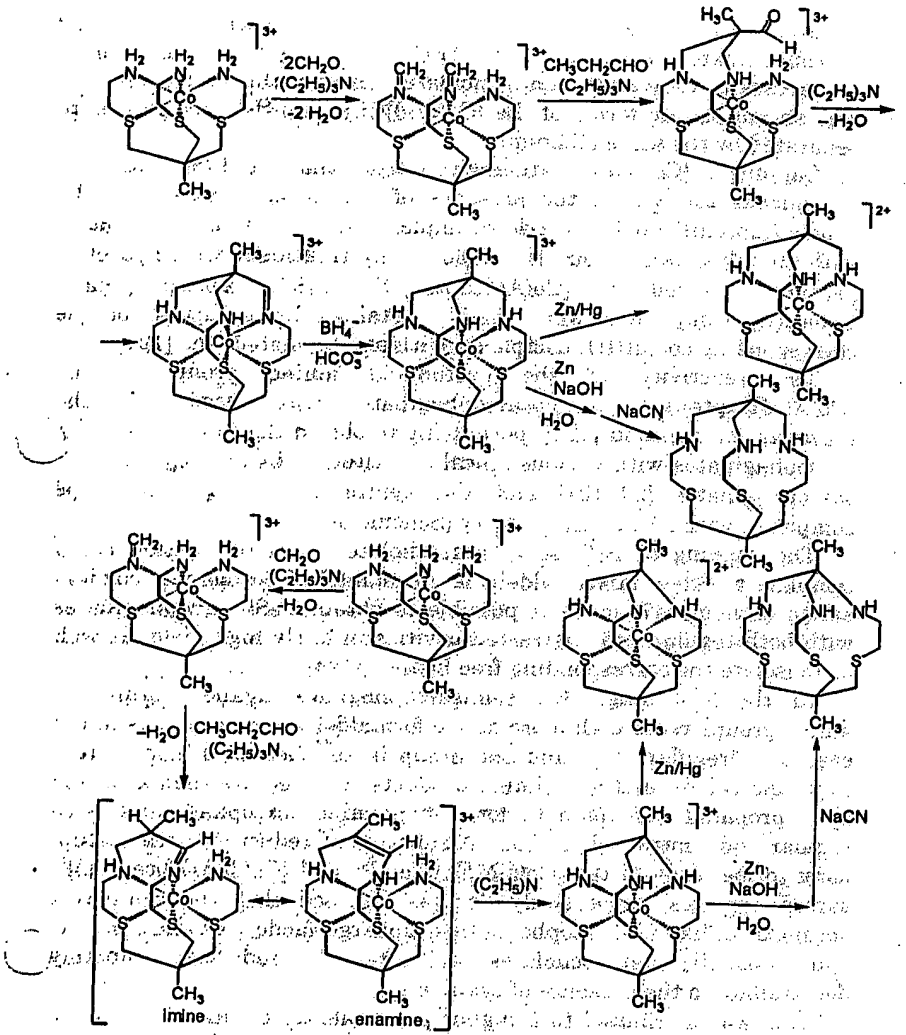
The reactivity of the protonated amino group in the $[Co(AMHcapten)]^{4+}$ aminosarcophaginate was used in the diazotization reaction [123], permitting to obtain the numerous $N_3S_3$ sarcophaginates with various apical substituents by analogy with $N_6$-sarcophaginates [94, 101] and also synthesize the *abcapten* type complexes with a contracted cavity (Scheme 46).

The capping of $N_3S_3$-semiclathrochelate $[Co(ten)]^{3+}$ cation *via* a template-assisted mixed aldehyde (formaldehyde/propanal) condensation (Scheme 47) made it possible to obtain $N_3S_3$-sarcophaginates with both regular and contracted cavities in fairly high yield, as well as to isolate the corresponding free ligands [124].

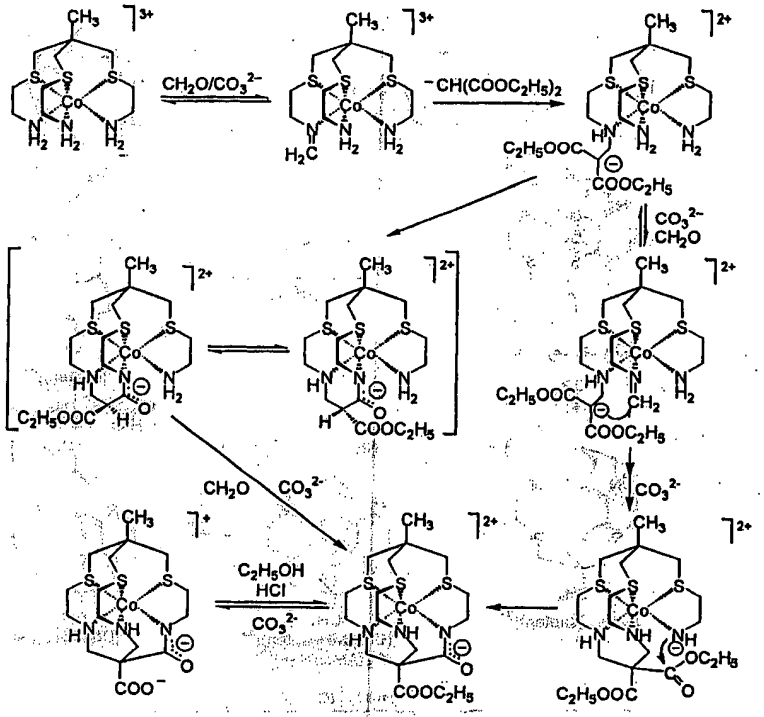
At the first stage, the semisarcophaginate ligand coordinated amino groups react with more active formaldehyde (two groups in the case of a "regular" cap, and one group in the case of a "contracted" cap), and the di- and monoimine products obtained are then attacked by a propanal carbanion to form monoimine sarcophaginates with regular and contracted cavities. A subsequent reduction with sodium borohydride leads to the $[Co(diMEcapten)]^{3+}$ and $[Co(diMEabcapten)]^{3+}$ sarcophaginates, respectively. It was stressed that the complexes obtained, unlike $N_6$-sarcophaginates, undergo facile reduction to low-spin cobalt(II) clathrochelates and after the reduction smoothly demetallate in the presence of cyanide anion.

This was attributed to a higher polarizability of thioether groups compared with that of amino groups, which leads to a decrease in the donor-acceptor interaction of thioether donors with first-row transition metals [124].

The cobalt(III) $N_3S_3$-oxosarcophaginates were obtained from $[Co(ten)]^{3+}$ semiclathrochelate with diethylmalonate (Scheme 48)



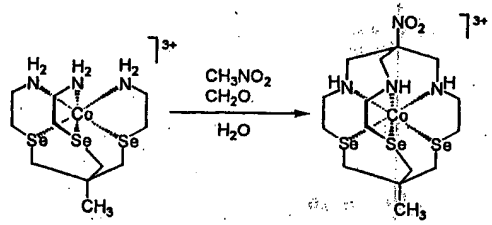

**Scheme 47**




**Scheme 48**

[123]. As with $N_6$-complexes [94, 101], other $N_3S_3$-oxosarcophaginates can also be synthesized using reactive amino groups of the $[Co(AMoxocapten)]^{2+}$ cation.

The first selenium donor atoms incorporating sarcophaginate was obtained starting from the initial cobalt(III) $N_3Se_3$-semiclathrochelate by condensation with nitromethane and formaldehyde in water (Reaction 37).

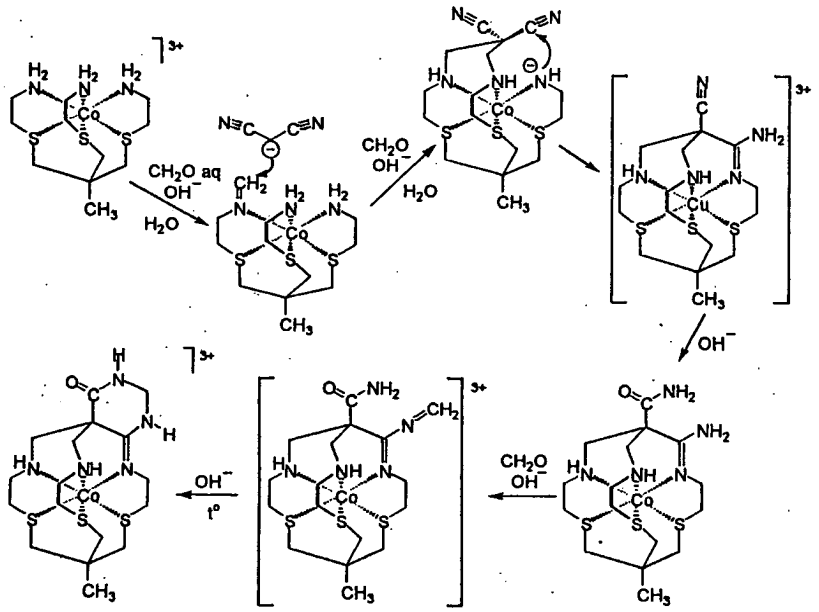



(37)

The following IEC separation (hydrochloric acid was used as eluent) and the vapor diffusion of ethanol into an aqueous solution of the cobalt(III) $N_3Se_3$-sarcophaginate led to the formation of $[Co(MENOsar\text{-}N_3Se_3)]Cl_3 \cdot 5H_2O$ crystals [125].

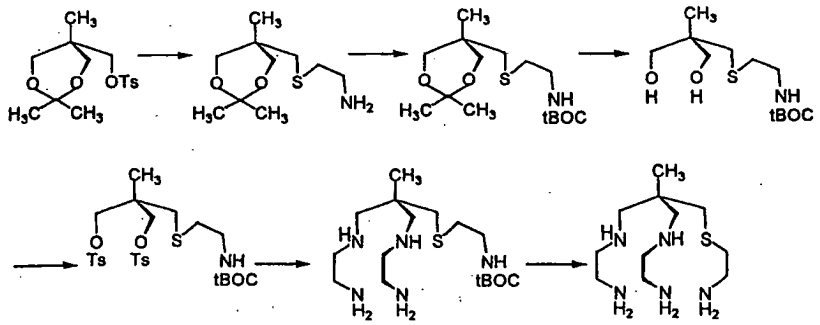
In the synthesis of amidine-functionalized cobalt(III) $N_3S_3$-sarcophaginates, malononitrile was used as a bifunctional carbon acid. The interaction of its pendant nitrile with the coordinated amino group of the $[Co(ten)]^{3+}$ semiclathrochelate led to the formation of an amidine $N_3S_3$-cage with an amide apical substituent.

This sarcophaginate originated from the nitriloamidine sarcophaginates, obtained at the first stage by a rapid intermolecular basic hydrolysis. The hydrolysis reaction was promoted by coordination to cobalt(III) ions. The resulting amide-substituted amidine sarcophaginates reacted with formaldehyde under basic conditions. The formaldehyde joined *exo*-nitrogen and the imine obtained then reacted with a neighboring deprotonated amide fragment forming a heterocycle (Scheme 49) [126].



**Scheme 49**





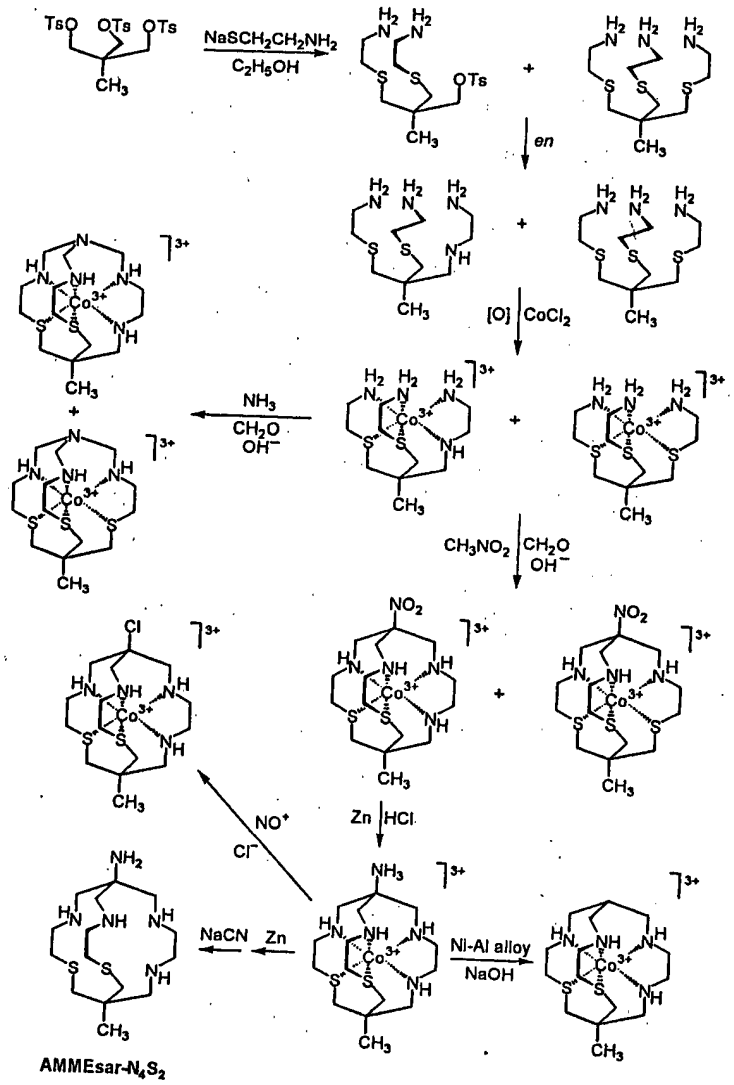
**Scheme 50**

The $N_5S$-semiclathrochelate ligand was prepared [127] according to Scheme 50. The interaction of this ligand with $Co^{2+}$ ions in methanol during oxidation by air oxygen and subsequent cross-linking with nitromethane and formaldehyde led to the formation of the $[Co(MENOsar\text{-}N_5S)](ClO_4)_3 \cdot H_2O$ sarcophaginate. The reduction of the latter by analogy with that for $N_6$-dinitrosarcophaginate resulted in the formation of the $[Co(MEAMHsar\text{-}N_5S)]Br_4 \cdot H_2O$ $N_5S$-sarcophaginate [127].

The analogous Scheme 51 was used for $N_4S_2$-sarcophaginate synthesis [128]. The mixture of the resultant $[Co(MENOsar\text{-}N_4S_2)]^{3+}$ and $[Co(MENOcapten)]^{3+}$ sarcophaginates was chromatographically separated. The reduction of the apical nitro group to a protonated amino group and subsequent diazotization reaction to produce $[Co(MECLsar\text{-}N_4S_2)](ClO_4)_3 \cdot 3H_2O$ and $[Co(MEsar\text{-}N_4S_2)](ClO_4)_3$ complexes were achieved. Free *AMMEsar*-$N_4S_2$ ligand was isolated after cobalt(II) complex reaction with cyanide anion and used for the synthesis of other ion complexes [128].

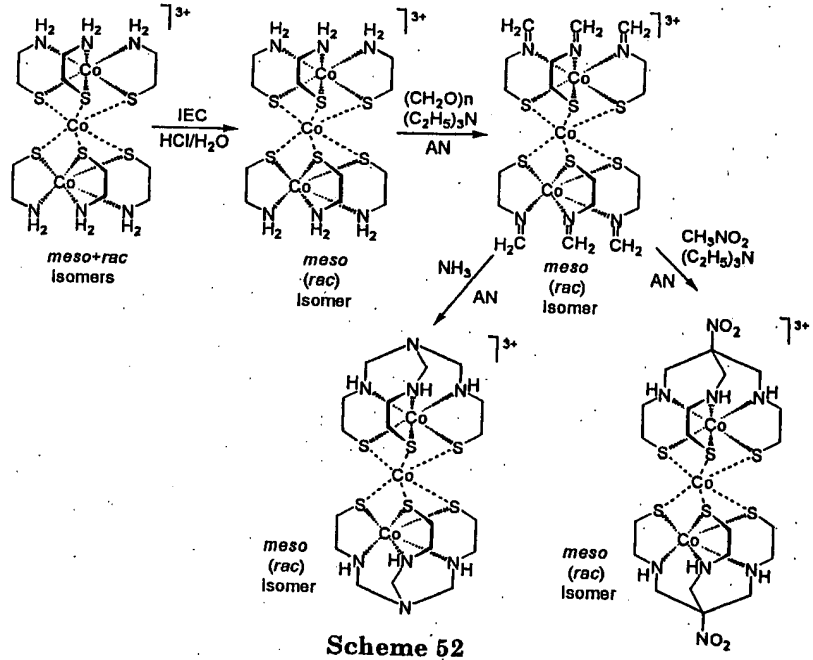
The first representatives of a new type of $N_3S_3$-sarcophaginates capped with *d*-metal ions were obtained starting from a trinuclear $[Co(Co(aet)_3)_2]^{3+}$ derivative of the 2-aminoethanethiol (Scheme 52). In this case, the kinetically inert central cobalt(III) ion served as a bifunctional capping agent. Both *rac*- and *meso*-forms of the initial complex were preliminarily isolated by IEC.

An attempt to carry out routine capping procedures with the $NH_3/CH_2O$ and $CH_3NO_2/CH_2O$ systems under basic conditions failed because of the occurrence of side reactions. Therefore, a stepwise

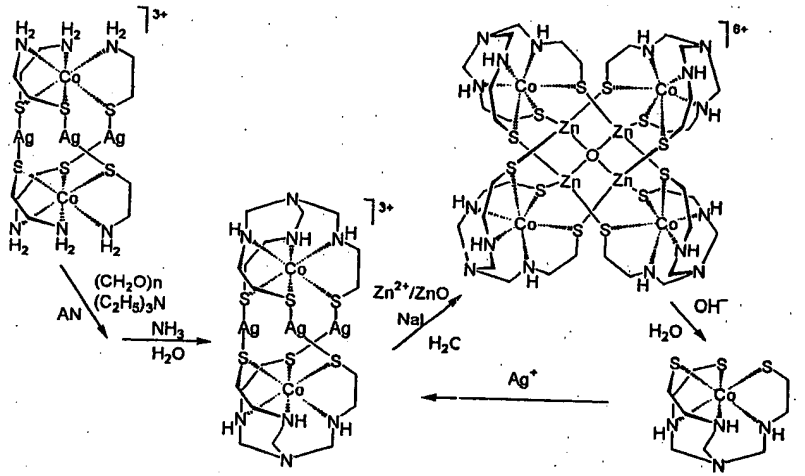



Scheme 51






Scheme 52

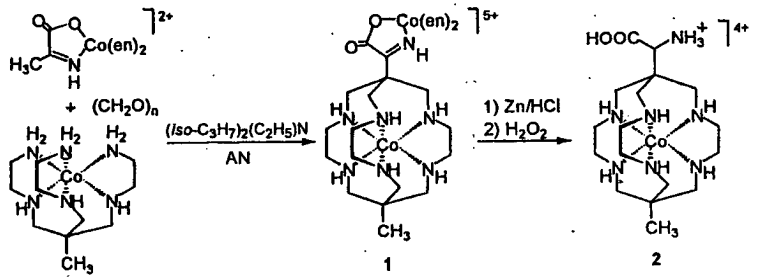



Scheme 53

synthesis of bis-sarcophaginates was implemented. At the first stage, the interaction of the $[Co(Co(aet)_3)_2]^{3+}$ cation with paraformaldehyde in the presence of triethylamine led to the hexaimine bis-semiclathrochelate. Then the compound obtained underwent capping with ammonia or nitromethane in the presence of triethylamine in catalytic amounts. In this case, the resulting clathrochelates retained the initial (*rac*- or *meso*-) configuration [129].

A similar strategy was employed to obtain mixed pentanuclear cobalt(III) and silver(I) $N_6S_6$-bis-sarcophaginates. The preliminarily synthesized $[Ag_3(Co(aet)_3)_2]^{3+}$ bis-semiclathrochelate [130] underwent condensation with paraformaldehyde in acetonitrile in the presence of triethylamine. A subsequent addition of aqueous ammonia led to the formation of a pentanuclear cobalt(III) bis-azasarcophaginate in high yield (Scheme 53) [131]. It was emphasized that the latter complex can also be obtained in a low yield by a routine procedure in aqueous solution. The resultant pentanuclear cobalt(III) bis-azasarcophaginate, when treated with zinc nitrate and oxide in water in the presence of NaI, formed an octanuclear $Zn_4Co_4$ aza-capped complex. This complex gave a cobalt(III) $N_3S_3$-semisarcophaginate under basic conditions [131].

In addition to ammonia and nitromethane, some other compounds containing active hydrogen atoms, such as bis-ethylenediamine cobalt(III) pyruvate, can be employed as capping agents for the synthesis of sarcophaginates [132]. The interaction of the trifluoromethanesulphonate salt of bis-ethylenediamine cobalt(III) pyruvate and $[Co(sen)]^{3+}$ semisarcophaginate with paraformaldehyde in acetonitrile in the presence of diisopropylethylamine gave a sarcophaginate containing bis-ethylenediamine cobalt(II) pyruvate in the apical position:



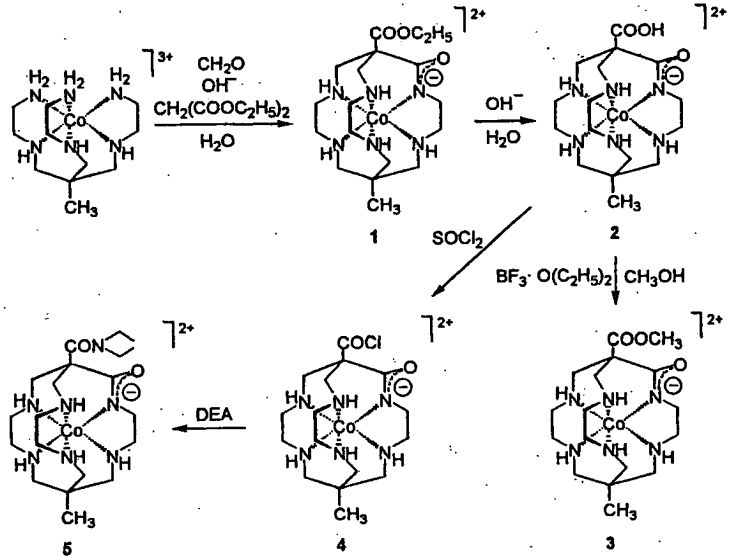

(38)



Reduction of complex **1** with zinc dust in aqueous hydrochloric acid followed by oxidation with hydrogen peroxide led to the formation of sarcophaginate **2**.

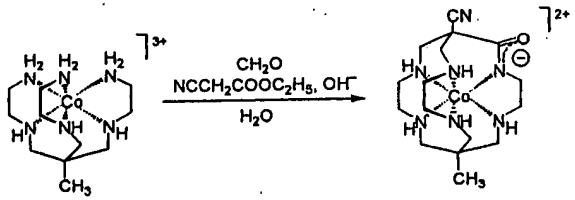
When diethylmalonate or cyanoacetate have been used instead of bis-ethylenediamine cobalt(III) pyruvate, the cobalt(III) oxoaza- and oxosarcophaginates were isolated by analogy with the previous scheme [133]. The semiclathrochelate $[Co(azasen)]Cl_3$ and $[Co(sen)]Br_3$ complexes, respectively, were used as initial compounds.

The interaction of $[Co(sen)]Br_3$ semiclathrochelate with formaldehyde and diethylmalonate in aqueous solution resulted in the $[Co(EFMEoxosar–H)](ClO_4)_2$ sarcophaginate **1**. The modification reactions of this complex resulted in clathrochelates **2-5** (Scheme 54). When the (+)- or (–)-isomer of $[Co(sen)]Br_3$ semisarcophaginate was used as initial complex, the corresponding $[Co(EFMEoxosar–H)](ClO_4)_2$ optical isomers were obtained. The reduction of $[Co(EFMEoxosar–H)](ClO_4)_2$ complex with zinc amalgam in aqueous solution led to the formation of the corresponding cobalt(II) complex [133].



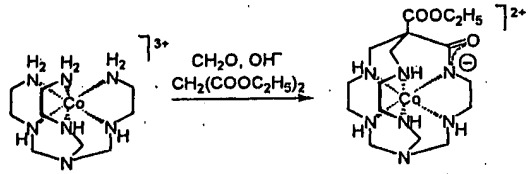

**Scheme 54**

When ethyl cyanoacetate was used instead of diethylmalonate, the macrocyclization reaction yielded mostly [Co(CNMEoxosar–H)]$^{2+}$ oxosarcophaginate with an apical nitrile group.




(39)

The [Co(azasen)]$Cl_3$ semisepulchrate underwent an analogous reaction with diethylmalonate [133]:




(40)

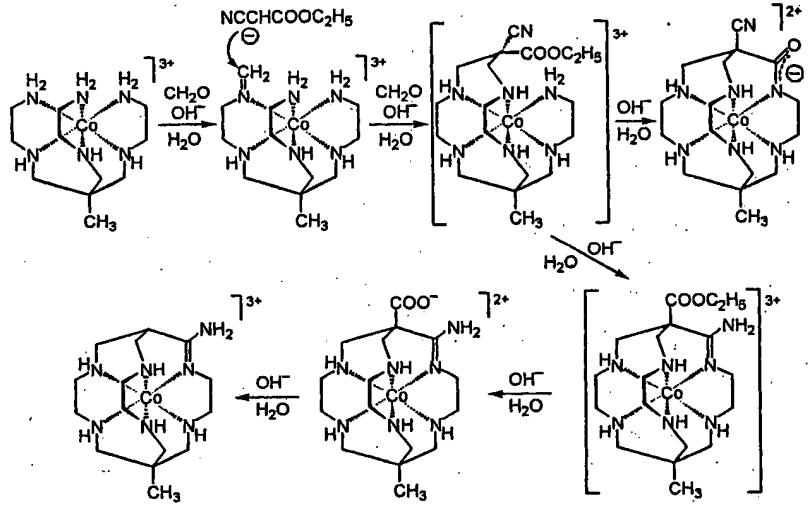
The *exo*-imine formed at the first stage *via* the addition of formaldehyde to the [Co(sen)]$^{3+}$ semisarcophaginate coordinated amino group condenses with an ethyl cyanoacetate anion through a deprotonated methylene unit. A second coordinated amino group follows the same condensation pathway, and then the remaining amino group condenses mainly with an ether group to give an amide fragment (Scheme 55). An attempt to isolate a free sarcophagine by demetallation of the cobalt(III) complex proved to be unsuccessful [134].

The amidine-functionalized cobalt(III) sarcophaginates with apical carboxylic acid and the complex resulting from its decarboxylation, as well as the [Co(MEazasar)]$^{3+}$ azasarcophaginate (formed by capping with ammonia resulting from the hydrolysis of the ethyl cyanoacetate nitrile groups), are minor clathrochelate products of this reaction [134].

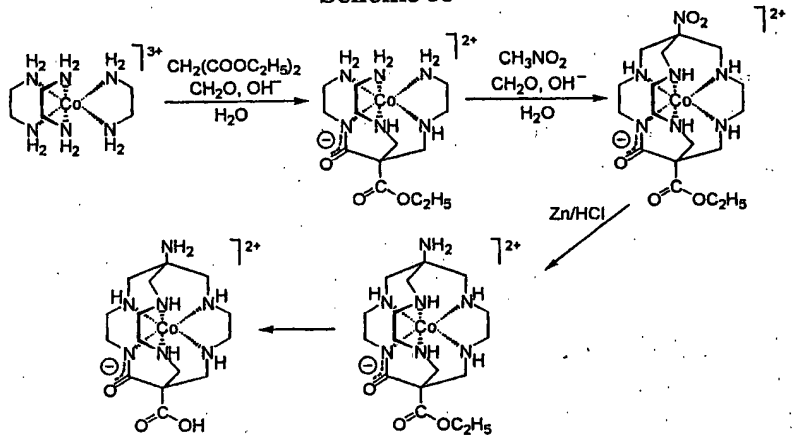
The [Co(EFoxosen–H)]$Cl_2$ semisarcophaginate, preliminarily synthesized by reaction of [Co(en)$_3$]$Cl_3$ tris-ethylenediaminate with diethylmalonate and formaldehyde, was capped with nitromethane in the presence of formaldehyde. The resultant nitrosarcophaginate underwent reactions involving both the apical groups (Scheme 56) [133].



The protons of alkyl groups in the α- and γ-positions relative to the pyridine nitrogen atom are, to a great extent, apt to be detached because of delocalization of a negative charge of the carbanion in the heterocycle. In the case of $NH^+$ salts and N-oxides, this tendency evidently increases.




**Scheme 55**




**Scheme 56**

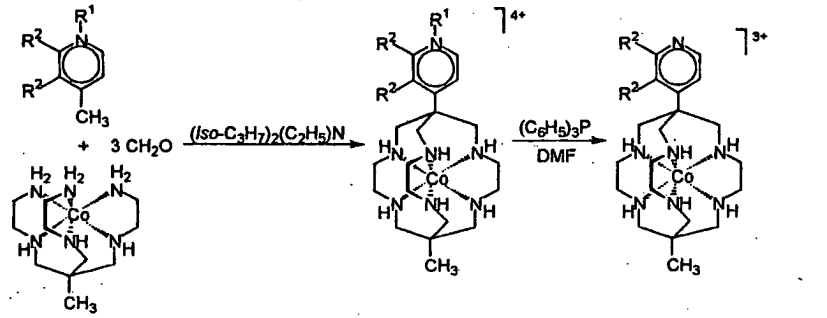
An attempt to utilize the reactivity of the methyl group protons of N-alkylated γ-picoline and γ-quinoline in the reaction of the semiclathrochelate $[Co(sen)]^{3+}$ cation with paraformaldehyde proved to be successful (Scheme 57).

The subsequent dealkylation of a heterocyclic nitrogen atom led to the formation of $[Co(MEPYsar)]Cl_4 \cdot 4H_2O$ and $[Co(MEQNsar)]Cl_4 \cdot 3H_2O$ sarcophaginates [135].

The facile reactions of the preliminarily synthesized semisarcophaginate with aromatic ketones and diketones and paraformaldehyde in acetonitrile allowed one to obtain polyfunctional aromatic substituted cobalt(III) sarcophaginates in high yields by Scheme 58.

Only one diimine cage complex was isolated with dibenzoylmethane (both carbonyl groups and one formaldehyde molecule are involved in its formation) while acetophenone formed two clathrochelates (imine and carbonyl-containing complexes) in a relatively high yield. Such imine sarcophaginates are readily reduced by $NaBH_4$, and the mixture of isomers induced by the chirality of a benzyl carbon atom has been formed in the case of a dibenzoylmethane derivative [136].

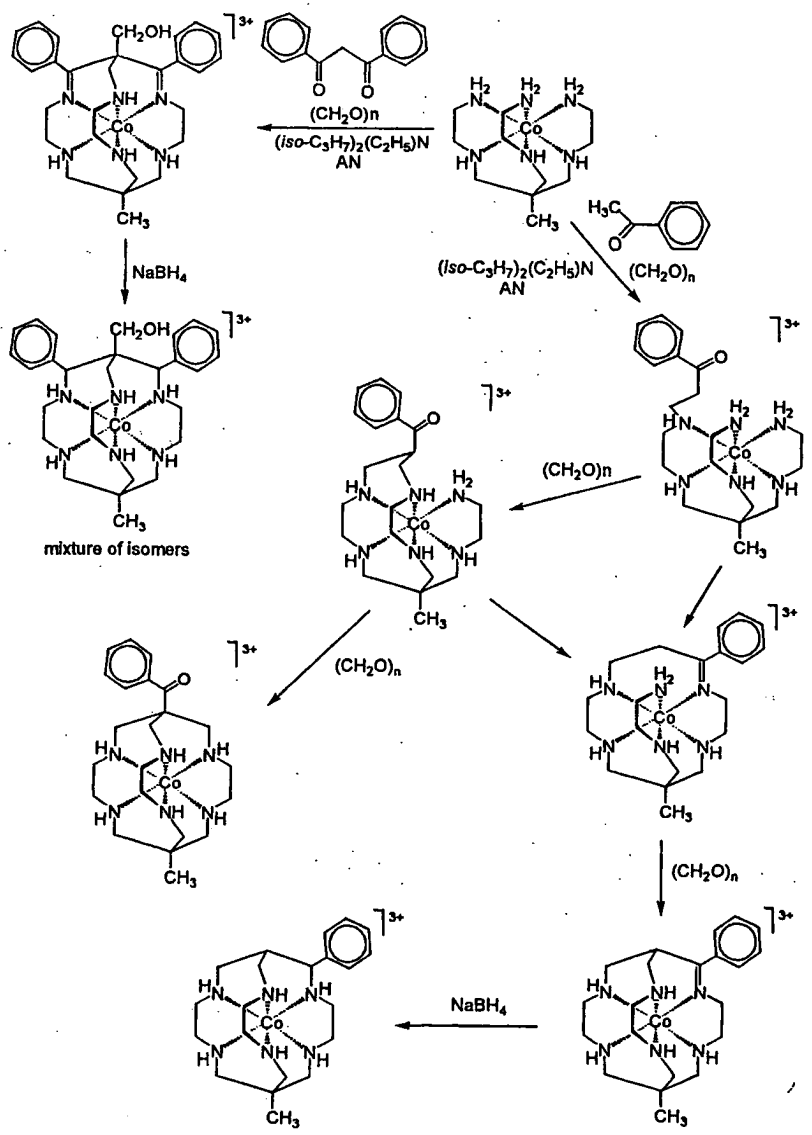
It was assumed that a methaneimine complex accepting a β-diketone carbanion is formed at the first stage of the dibenzoylmethane derivative synthesis. Two ketone groups would then undergo condensation with the remaining deprotonated primary




2; $R^1=CH_3$, $R^2=H$ $[Co(ME(N\text{–}mePY)sar)]^{4+}$
3; $R^1=CH_2C_6H_5$, $R^2=H$ $[Co(ME(N\text{–}bnPY)sar)]^{4+}$
4; $R^1=CH_3$, $2R^2=[CH]_4$ $[Co(ME(N\text{-}meQN)sar)]^{4+}$
5; $R^1=CH_2C_6H_5$, $2R^2=[CH]_4$ $[Co(ME(N\text{-}bnQN)sar]^{4+}$
6; $R^2=H$ $[Co(MEPYsar)]^{3+}$
7; $2R^2=[CH]_4$ $[Co(MEQNsar)]^{3+}$

**Scheme 57**






**Scheme 58**

amino groups of the semiclathrochelate. The tertiary capped carbon atom activated by two imine groups reacts with a formaldehyde molecule to give the apical methoxyl substituent.

In the case of an acetophenone derivative, the reaction also involves the formation of a methaneimine complex that has undergone intermolecular reaction with the carbanion. Two processes may then take place: an intramolecular condensation with the two remaining methaneimine fragments of the same molecule to yield a $C_3$-symmetric apical functionalized sarcophaginate and a reaction of the ketone group with the remaining deprotonated primary amino groups to give meridional-substituted imine sarcophaginate [136].

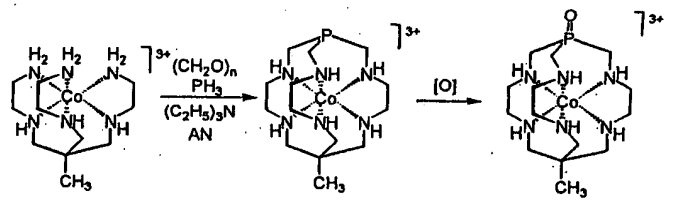
A more detailed synthesis of 4-nitrophenyl-, 2-naphthyl-, 2-phenanthryl-, 9-anthryl-, and 2-anthraquinonyl-substituted cobalt(III) rcophaginates starting from the corresponding methylarylketones was reported in Ref. 137.

In all cases, except for 9-acetylanthracene, both $C_3$-symmetric amine clathrochelates with apical aromatic substituents and $C_3$-nonsymmetric imine sarcophaginates with substituents in the methylene units have been formed (Scheme 59). The reaction of 9-acetylanthracene under the same conditions led only to the aroyl-type sarcophaginate, since in this case a bulky substituent inhibits the condensation of a keto group with an amino group to give imine.

Both types of compounds obtained were reduced with $NaBH_4$ in aqueous solution (except the anthraquinone imine complex, which under given conditions an aryl substituent has been reduced). The resultant 4-nitrophenylsarcophaginate with substitution in the methylene unit was further reduced to a 2-aminophenyl-substituted clathrochelate with metallic tin in aqueous HCl.

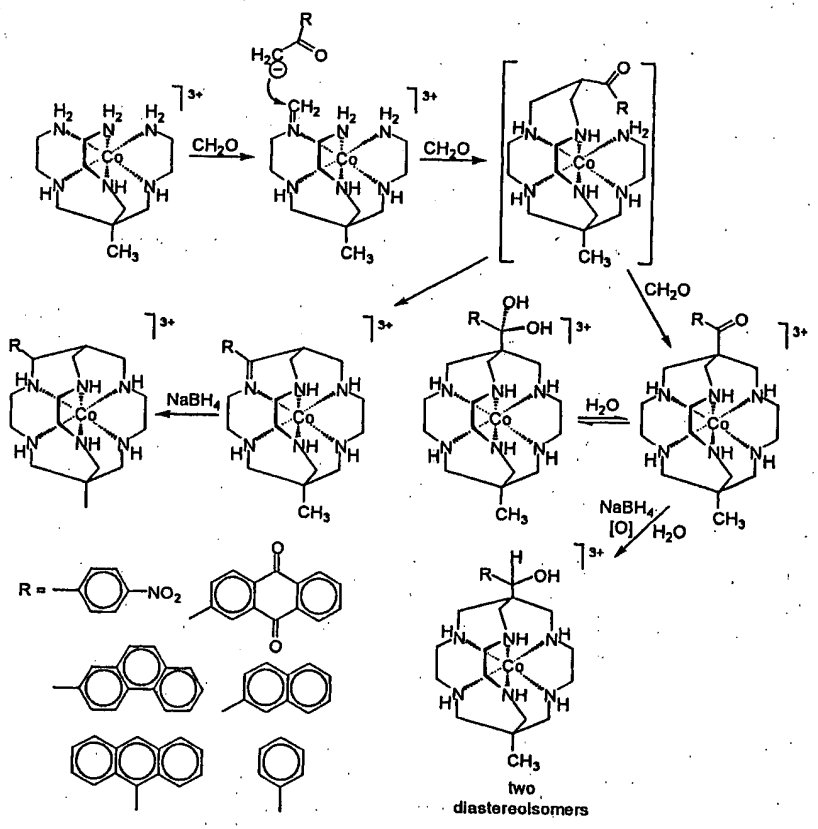
Since the hydrogen atoms in phosphorus(III) and antimony(III) hydrides are also active, these compounds have been used as capping agents for cobalt(III) semiclathrochelates. The reaction of the $[Co(sen)](CF_3SO_3)_3$ complex with an excess of paraformaldehyde, phosphine, and triethylamine in acetonitrile at room temperature resulted in a phosphorus-containing $[Co(MEphosphasar)]^{3+}$ sarcophaginate, which was readily oxidized to $[Co(MEOphosphasar)]^{3+}$ cation with air oxygen or hydrogen peroxide in aqueous solution [138]:





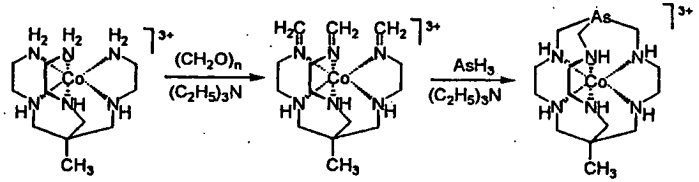

(41)

Arsine is a less reactive capping agent, and tris-imine complex was preliminarily obtained by reaction of the $[Co(sen)]Cl_3$ semisarcophaginate with an excess of paraformaldehyde in




**Scheme 59**

acetonitrile, catalyzed by triethylamine. After treatment of the reaction mixture with aqueous hydrochloric acid, the yield of the imine $[Co(sim)]Cl_3$ complex was 95%. The trifluoromethanesulphonic salt of a $[Co(sim)]^{3+}$ cation was reacted with arsine in the presence of triethylamine to form an arsine-capped sarcophaginate in good yield:




(42)

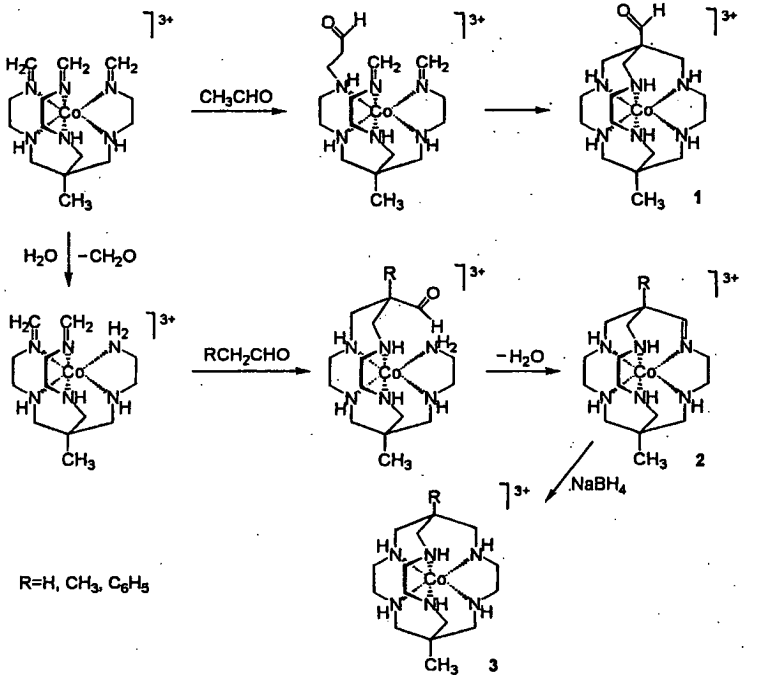
This complex was isolated from the reaction mixture by IEC after treatment with hydrochloric acid [139].

A novel strategy for the synthesis of sarcophaginates is based on the interaction of the $[Co(sim)]^{3+}$ complex with other primary aldehydes, in particular, acetaldehyde [140]. The reaction carried out in acetonitrile in the presence of triethylamine yielded the two main products, aldehyde sarcophaginate **1** and imine complex **2**, Scheme 60. The latter resulted from the removal of formaldehyde in the presence of water to give a diimine complex that reacted with aldehyde. The reduction of imine clathrochelate **2** with $NaBH_4$ yielded saturated sarcophaginate **3**. A template condensation of $[Co(sen)]^{3+}$ semisarcophaginate with two equivalents of formaldehyde and one equivalent of acetaldehyde also produced imine complex **2** in a good yield. A novel strategy for sarcophaginate synthesis was also extended for the preparation of complexes with other substituents at the apical carbon atom [140].

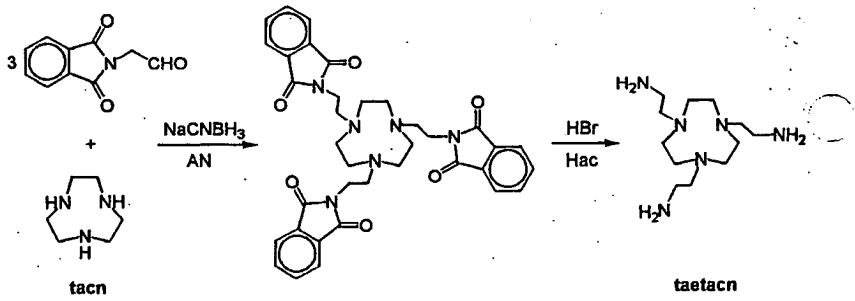
The reactivity of aldehyde groups was also used for the synthesis of the long-chain cobalt (III) sarcophaginates, which display anthelmintic properties [110, 141].

Semiclathrochelate complexes containing macrocyclic fragments have been employed in the synthesis of sarcophaginates with apical macrocyclic rings. Such macrotricyclic cobalt(III) compounds were obtained starting from the macrocyclic hexamine *taetacn* precursor [142]. This precursor was preliminarily synthesized by reductive alkylation of 1,4,7-triazacyclononane *(tacn)* with phthalimidoacetaldehyde in the presence of $NaNCBH_3$. The desired product was





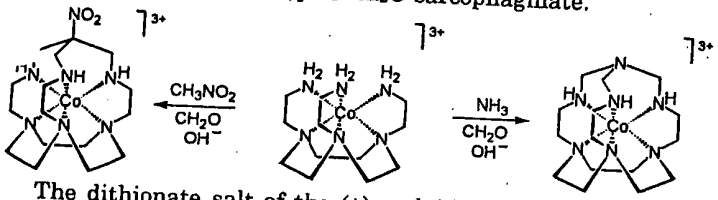

**Scheme 60**




**Scheme 61**

obtained by acidic hydrolysis of the protecting phthaloyl groups (Scheme 61).

A mixture of a crude *taetacn*·6HBr, $CoCl_2 \cdot 6H_2O$, NaOH and activated carbon in water was air-bubbled followed by treatment with an excess of $NaClO_4$ to give a mixture of semiclathrochelate Λ- and Δ-$[Co(taetacn)](ClO_4)_3$ isomers. This mixture was separated by eluation with aqueous sodium (+)-tartrate on an ion-exchange column. The free ligand was readily obtained upon demetallation of the purified complex with $H_2S$ [142]. The capping of $[Co(taetacn)]^{3+}$ cation with nitromethane and formaldehyde in aqueous solution in the presence of $Na_2CO_3$ followed by separation on an ion-exchange column yielded a racemic $[Co(NOsartacn)]Cl_3 \cdot 2H_2O$ sarcophaginate.



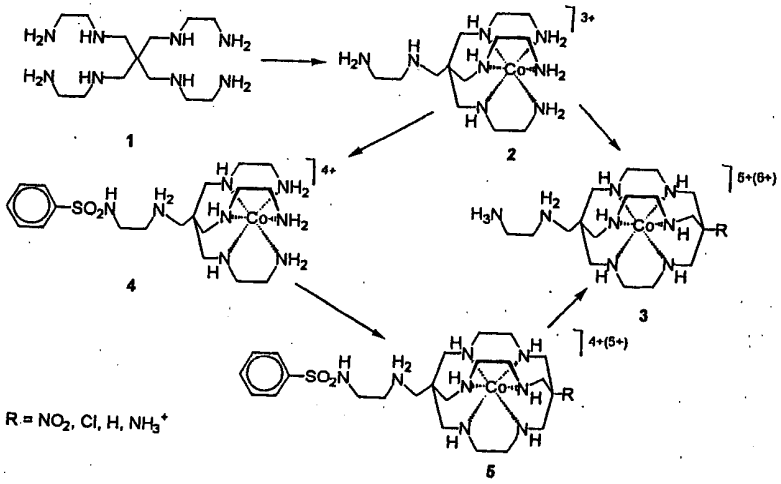

(43)

The dithionate salt of the (+) and (–)-$[(Co(NOsartacn)]^{3+}$ trication was resolved using aqueous sodium-antimony (+)-tartrate as an eluents. The reduction of $[Co(NOsartacn)]Cl_3 \cdot 2H_2O$ complex with zinc dust in aqueous hydrochloric acid followed by treatment with hydrogen peroxide led to the formation of the $[Co(AMHsartacn)]^{4+}$ aminosarcophaginate. This complex was separated into optically active forms by the same procedure [142].

The racemic $[Co(azasartacn)]Cl_3 \cdot 1/2CH_3OH \cdot C_2H_5OH$ complex resulted from capping of $[Co(taetacn)]^{3+}$ cation with ammonia and formaldehyde in aqueous solution in the presence of lithium carbonate. Only partial separation was achieved when attempts were made to resolve azasarcophaginate $[Co(azasartacn)]^{3+}$ cation into Λ- and Δ-forms IEC. Therefore, the pre-resolved Λ- and Δ-$[Co(taetacn)](ClO_4)_3$ semiclathrochelates were used as initial compounds. As result, the Λ- and Δ-$[Co(azasartacn)]^{3+}$ sarcophaginates were isolated as $PF_6^-$ salts and were additionally purified by fractional crystallization from aqueous solution [142].

Semiclathrochelate $N_3S_3$- and $N_6$-complexes with one of the tetrapodal units as apical substituent were prepared by the interaction of cobalt(III) ion with potentially octadentate tetrapodal $N_4S_4$- and $N_8$-ligands (Scheme 62). Cyclization of these complexes



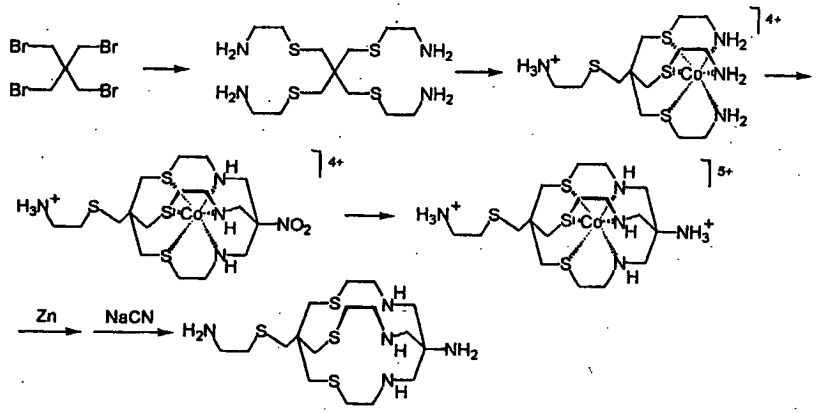



**Scheme 62**

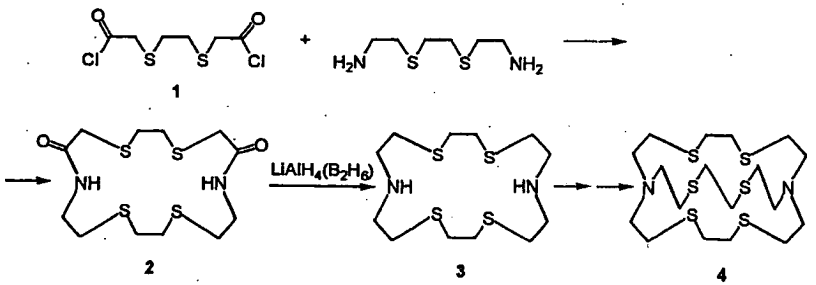
with nitromethane yielded so-called reinforced sarcophaginates apt to undergo reaction with participation of the nitro group and a reinforcing substituent. For instance, as a result of the above reactions, the tetrapodal 5,5'-bis-(4-amino-2-azabutyl)-3,7-diazanonane-1,9-diamine **1**, preformed *via* reaction of ethylenediamine with pentaerythritotosylate, gave sarcophaginate **3** containing apical ethylenediamine fragments [143].

The $N_3S_3$-containing analog of sarcophaginate **3** was obtained from 5,5'-bis-(4-amino-2-thiabutyl)-3,7-dithianonane-1,9-diamine by Scheme 63 [144]. After reduction with zinc dust the resultant $N_3S_3$-sarcophaginate underwent demetallation with NaCN. Thus, the ligand obtained may be employed for the synthesis of other metal ion complexes.

The synthesis of $S_6$-sepuchrate was primarily performed by Lehn and coworkers [145] *via* condensation of dithiadiamine and chloroanhydride of dithiadicarboxylic acid under high-dilution conditions to produce macrocyclic diamide **2** which after reduction to corresponding diamine **3** was built up to macrobicyclic ligand **4** (Scheme 64).



Scheme 63



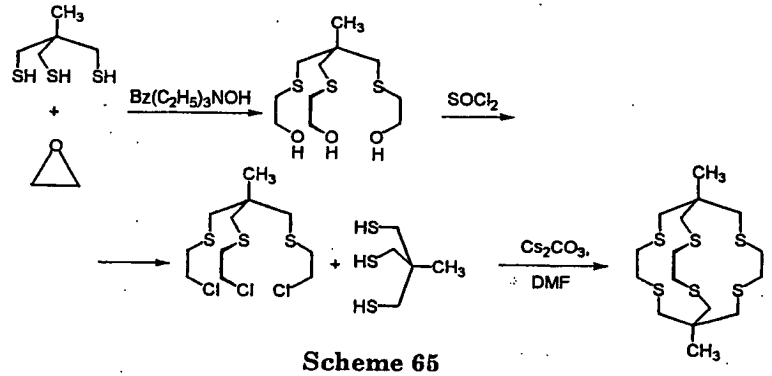
Scheme 64

The first cobalt(II) and cobalt(III) $S_6$-sarcophaginates were obtained by Sargeson and coworkers [146] from the preliminarily synthesized free *diMEsar-S6* ligand (Scheme 65).

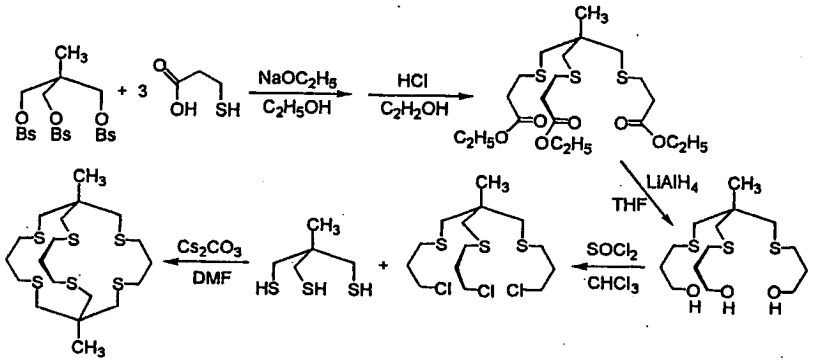
A caesium ion was used as the template in this synthesis. The resultant ligand easily formed a cobalt(II) complex in methanol-methylene dichloride mixture. The isolated $[Co(diMEsar\text{-}S_6)](CF_3SO_3)_2$ clathrochelate was readily oxidized by $AgCF_3SO_3$ in aqueous solution to the cobalt (III) $[Co(diMEsar\text{-}S_6)](CF_3SO_3)_3$ $S_6$-sarcophaginate [146].

The expanded $S_6$-sarcophaginate *diMEl,3pnsar-S6* ligand displaying high conformational lability and, therefore, apt to be readily demetallate, was synthesized by Scheme 66 [147].





Scheme 65

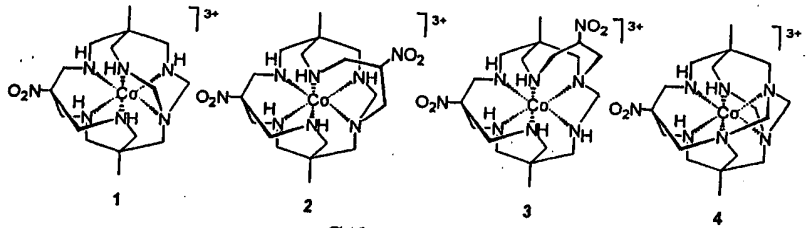


Scheme 66

The interaction of the free ligand with cobalt(II) perchlorate in the presence of $AgClO_4$ as a precipitant in the nitromethane-methanol mixture made it possible to isolate the $[Co(diME\ 1,3pnsar\text{-}S_6)](ClO_4)_3$ clathrochelate. The reduction of this clathrochelate with sodium dithionate led to the formation of a cobalt (II) complex that readily produced a free sarcophagine [147].

Sarcophaginates can also be prepared by template condensation of bis-triamine metal complexes with formaldehyde and nitromethane or ammonia. Macrotricyclic and macrotetracyclic complexes of different structures have simultaneously been formed [148, 149].

Treatment of $[Co(tame)_2]^{3+}$ cation (where *tame* is 1,1,1-tris-(aminomethyl)ethane) in aqueous solution at pH 10.5 with formaldehyde and nitromethane gave mainly a macrotricyclic $[Co(NOtrisartame)]^{3+}$ cation **1** in high yield (*ca* 50%), isolated as a



Scheme 67

[Co(NOtrisartame)](ZnCl$_4$)Cl·0.5H$_2$O complex. Two other macrocyclic complexes **2** and **3** with different rings (Scheme 67) were isolated in much lower yield (*ca* 10%) [149].

The reduction of sarcophaginate **1** with zinc dust under acidic conditions converted the apical nitro group into an amino substituent with cleavage of the four-membered rings and extrusion of the $Co^{2+}$ ion.

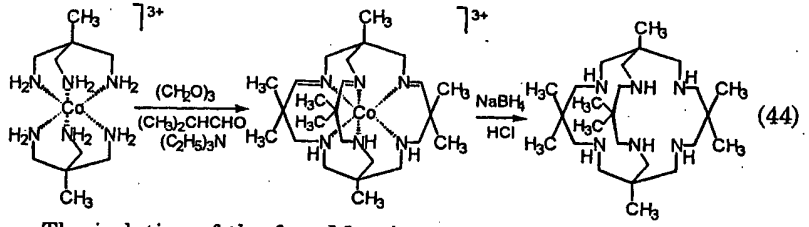
The use of ammonia instead of nitromethane in the template condensation with $[Co(tame)_2]^{3+}$ cation gave the macrotricyclic $[Co(azatrisartame)]^{3+}$ heptazasarcophaginate (yield *ca* 30%). Like its nitromethane analog, this complex is remarkably stable in aqueous hydrochloric acid. Furthermore, treatment of $[Co(azatrisartame)]^{3+}$ cation with trifluoromethanesulphonic acid for several days resulted in a triimine complex (*ca* 80%) with a ruptured *aza*-cap, but the methylene units and the four-membered rings remained unaffected [149].

One more product of the condensation of $[Co(tame)_2]^{3+}$ with nitromethane and formaldehyde with a yield of *ca* 10% was identified in Ref. 148 as macrotetracyclic [Co(NOtetrasartame)]Cl$_3$·3H$_2$O sarcophaginate **4**. Its reduction with zinc dust in aqueous hydrochloric acid resulted in the corresponding cobalt(II) $[Co(AMtetrasartame)]^{2+}$ aminosarcophaginate, which can either oxidize to a cobalt(III) complex or demetallate with hydrochloric acid to cleave four-membered chelate fragments. Both macrotetracyclic cobalt(III) complexes are remarkably stable to hydrolysis in acidic (6 molar hydrochloric acid at 60°C) and mildly basic (pH < 9 at 25°C) conditions, although they decompose at pH >9.

A bis-triamine $[Co(tame)]^{3+}$ complex also reacted with formaldehyde and aldehydes of carboxylic acids RCHO (where R is CH$_3$, C$_2$H$_5$, or (CH$_3$)$_2$CH)) to form cobalt (III) triiminosarcophaginates



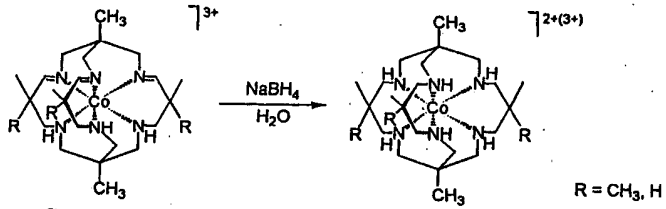
with an expanded cavity, which after their reduction with NaBH$_4$, were demetallated with hydrochloric acid:



(44)

The isolation of the free *Mestricosasar* ligand enabled a variety of transition metal complexes to be synthesized and studied [150].

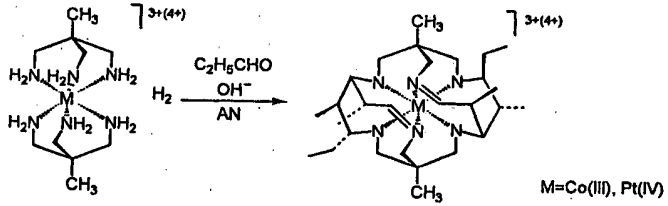
The reduction of triimine sarcophaginate $[Co(Me_8tricosatrienesar)]^{3+}$ and $[Co(Me_5tricosatrienesar)]^{3+}$ cations with NaBH$_4$ in aqueous solution at pH 10 led to the formation of saturated cobalt(II) and cobalt(III) sarcophaginates [151]:



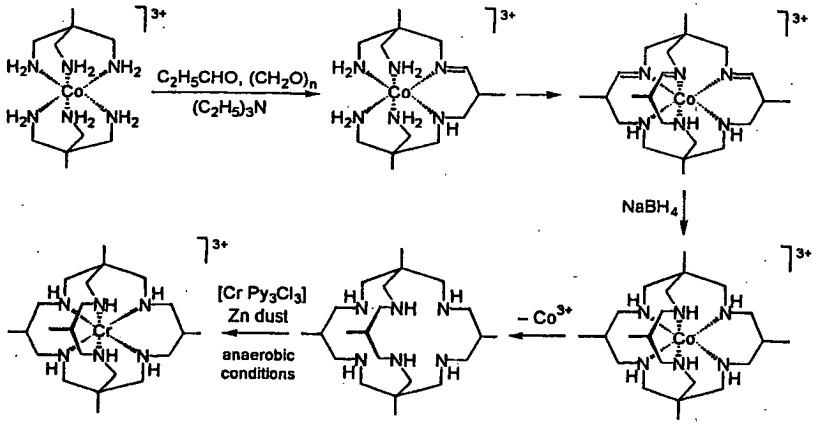
(45)

Condensation of $[Co(tame)_2]^{3+}$ cation with propanal is described in more detail in Ref. 152. The resultant $[Co(fac\text{-}Me_5tricosanesar)]^{3+}$ sarcophaginate was demetallated, and the free ligand was employed for the synthesis of a chromium(III) sarcophaginate with unusual spectral characteristics (Scheme 68) [153].

The $[Co(tame)_2]^{3+}$ and $[Pt(tame)_2]^{4+}$ bis-triaminates underwent a template condensation with propanal under basic conditions to give with remarkable regio- and stereo-selectivities rigid sarcophaginates with an expanded cavity [154].



(46)

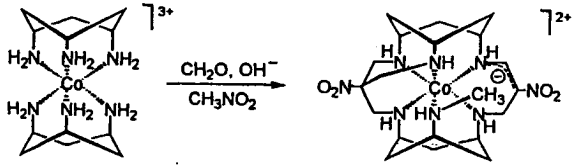



**Scheme 68**

The two pairs of protonated units condense with amino groups to form six-membered chelate cycles (the so-called "straps") cross-linking two *tame* fragments to produce two tetradentate moieties. The two remaining primary amine groups, being in the *trans* position, then condense with propanal to form bridges ("cross straps") between straps.

As a result, a rigid cage structure involving fourteen chiral sites (ten carbon atoms and four secondary nitrogen atoms of the framework) was obtained [154].

Condensation of $[Co(tacn)_2]^{3+}$ bis-triaminate with formaldehyde and nitromethane led to an unusual clathrochelate complex with a stable carbanion. A tripodal cap from three formaldehyde and one nitromethane species formed on one octahedral face as expected by the conventional route. However, on another octahedral face, the capping process proceeded in an unusual way to stabilize a carbanion chelate and to methylate the remaining coordinated amino group:




(47)

An intermediate carbanion cycle is stable because of coordination to cobalt(III) ion and charge delocalization in the six-membered



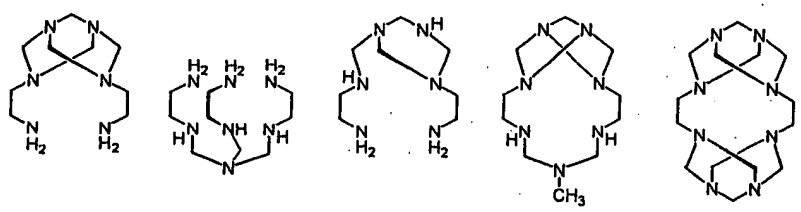
nitro group-containing chelate cycle. The further condensation to yield a tripodal capping fragment does not take place. Methylation of a coordinated amino group of the *tacn* moiety accomplished this process [155].

The platinum(IV), rhodium(III), and iridium(III) sepulchrates, dinitrosarcophaginates, and diaminosarcophaginates have been synthesized in high yields (45–65% for Pt(IV), 40% for Ir(III), and 90–100% for Rh(III)) starting from their tris-ethylenediaminates [94, 156, 157]. The rhodium(III) and iridium(III) complexes were prepared in a similar manner to that for cobalt (III) complexes, except of the elevated temperatures (Rh, 60°C; Ir, 90°C) required for the quoted yields. Moreover, if chiral $[Rh(en)_3]^{3+}$ cation was used initially, clathrochelate complexes were obtained in *ca* 100% chemical and chiral yields, despite the seven centres of chirality [157].

Recrystallization of the $[Pt(diNOsar–H)]Cl_3 \cdot 3H_2O$ complex from a 1:1 diluted hydrochloric acid gave the $[Pt(diNOsar)]Cl_4 \cdot 3H_2O \cdot HCl$ sarcophaginate. It was initially suggested [156] that reduction of this complex with $SnCl_2$ solution in 1:1 diluted hydrochloric acid yields a $[Pt(diAMsar)]Cl_4 \cdot 2H_2O$ clathrochelate. However, the X-ray diffraction data indicate that the complex obtained is actually a dihydroxylamine $[Pt(diNHOHsar)]Cl_4 \cdot 2H_2O$ sarcophaginate. Its recrystallization from hot trifluoromethanesulphonic acid resulted in the $[Pt(diNHOHsar)](CF_3SO_3)_4 \cdot 4H_2O$ compound.

Attempts of Sargeson and coworkers [158] to cross-link the chromium(III) tris-ethylenediaminate have not been successful because of rapid dissociation of intermediate imine species. However, Endicott and coworkers [159] have managed to synthesize chromium(III) sepulchrate, not isolating its tris-ethylenediaminate, upon heating of anhydrous chromium sulphate with concentrated aqueous ethylenediamine for several hours followed by the addition of formaldehyde and ammonia with constant heating. The $[Cr(sep)](ClO_4)_3$ sepulchrate was isolated from the reaction mixture in 10% yield by IEC.

The template synthesis of the nickel sepulchrate proved to be rather complicated because of macrocyclic and acyclic amines (Scheme 69), competitive formation reactions occurred upon refluxing ethylenediamine, formaldehyde, and ammonia in the presence of $Ni^{2+}$ ion.



1 2 3 4 5

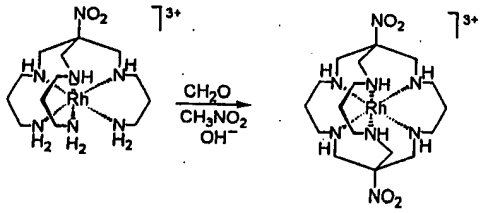
**Scheme 69**

Nevertheless, after precipitation of the major reaction products (the nickel(II) complex with ligand **1**, yield *ca* 90%, and a complex with *azasen* ligand **2** as perchlorate salts). $[Ni(sep)](ClO_4)_2$ sepulchrate was isolated from the solution by fractional crystallization (yield *ca* 1%) [160]. Attempts to obtain the nickel(II) sepulchrate from the preformed $[Ni(azasen)](ClO_4)_2$ semisepulchrate have not been successful. However, the free *azasen* ligand isolated is essential for the synthesis of clathrochelate complexes of other metal ions.

The use of 1,2-diaminopropane instead of ethylenediamine in the condensation on the nickel(II) ion matrix also leads to the formation of the nickel(II) complex with the corresponding semiclathrochelate ligand [161].

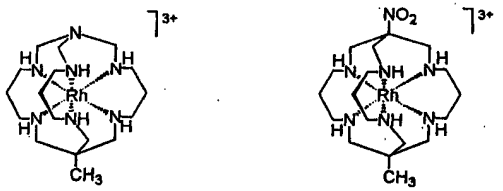
Condensation of $[Cu(en)_2]^{2+}$ cation with nitromethane and formaldehyde yielded copper(II) complexes with macrocyclic and polydentate nitrogen-containing ligands, though a copper(II) sarcophaginate was not isolated [162, 163].

When 1,3-propanediamine semiclathrochelates have been used instead of ethylenediamine derivatives, the encapsulation of large metal ions in low oxidation states predominated. For instance, the rhodium(III) sarcophaginate was obtained by template condensation of the corresponding semiclathrochelate with formaldehyde and nitromethane in a high yield [5]:



(48)





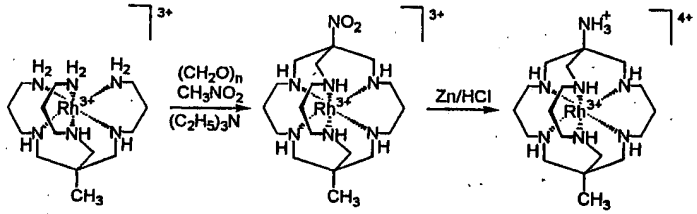
1 2

**Scheme 70**

The synthesized complex was easily reduced to the rhodium(II) sarcophaginate. The rhodium sarcophaginates **1** and **2** with other apical substituents were also prepared (Scheme 70).

The synthetic procedure for these complexes in acetonitrile with paraformaldehyde as a cross-linking agent is described in more detail in Ref. 164.

A standard procedure was also employed to isolate the $[Rh(MEAMHsar)](CF_3SO_3)_4$ aminosarcophaginate.



(49)

Attempts to synthesize the clathrochelate complexes of lanthanide ions *via* template condensation of the tripodal amine *tren* with formaldehyde bis-(dimethylamino)methane derivative on the rare-earth metal ion were successful only for ytterbium. The $[Yb(metr)](CF_3SO_3)_3 \cdot AN$ clathrochelate was obtained in 3–5% yield [165]. With ytterbium cation, as well as with cerium, praseodymium, europium, yttrium, and lanthanum ions, the major reaction products proved to be mono- and dibridged semiclathrochelate complexes with ligands **1** and **2** (Scheme 71).

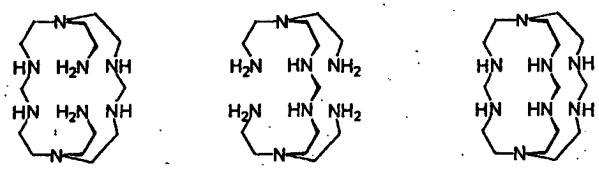
As mentioned above, a template synthesis is a very efficient approach to the preparation of sarcophaginates and sepulchrates of certain metals. For all other metal ions, this synthetic pathway is inapplicable or gives the desired products in low yields. For instance, the yields of nickel(II) and chromium(III) sepulchrates resulting from template condensation are only *ca* 1 and 10%, respectively. This problem can largely be overcome if the synthesis of a variety of metal

sarcophaginates performs from free ligands obtained by demetallation of the corresponding cobalt(II) complexes with concentrated HBr and HCl at 130÷150°C. This synthetic pathway has been employed for the isolation of free *sar* and *diAMsar* ligands.

The clathrochelate $[Cr(diAMsar)]Cl_3 \cdot 3H_2O$ complex was synthesized by reaction of free *diAMsar* ligand with $CrCl_3$ in dry DMF in the presence of zinc powder. The use of free *sar* ligand instead of *diAMsar* ligand and treatment of the reaction mixture with aqueous $NaCF_3SO_3$ resulted in a $[Cr(sar)](CF_3SO_3)_3$ sarcophaginate. The encapsulation of the inert chromium(III) ion by the macrobicyclic ligand has accomplished *via* trace amounts of the labile $Cr^{2+}$ ion generated by metallic zinc, followed by rapid oxidation to chromium(III) clathrochelate. Chromium(II) compounds have not been isolated because of their low stability [158]. The chromium(III) $[Cr(AMHMEsar\text{-}N_5S)]Br_4 \cdot 3H_2O$ $N_5S$-sarcophaginate was synthesized by an analogous route [166].

The reaction of vanadium(III) $V(acac)_3$ acetylacetonate with free *diAMsar* ligand in aqueous ethanol at 40°C for three days led to the formation of a vanadium(IV) $[V(diAMHsar–2H)](S_2O_6)_2 \cdot 2H_2O$ sarcophaginate. The central ion presumably was oxidized by air oxygen. The isolated complex is stable over a wide pH range (1÷10) but decomposes in the presence of oxidants [167].

Like vanadium(IV) and chromium(III) sarcophaginates, ruthenium(II) complexes have readily been obtained from free ligands. The initial $[Ru(DMF)_6](CF_3SO_3)_2$ solvato-complex was prepared by treating $[Ru(H_2O)_6](CF_3SO_3)_2$ salt with pure DMF under argon followed by dehydratation with triethyl orthoformate, concentration of the solution, and crystallization at –20°C. Prolonged reflux (2 days) of this solvato-complex and free *sar* ligand in dry ethanol in a strictly oxygen-free atmosphere resulted in a *ca* 60% yield of the $[Ru(sar)](CF_3SO_3)_2$ sarcophaginate, extremely sensitive to

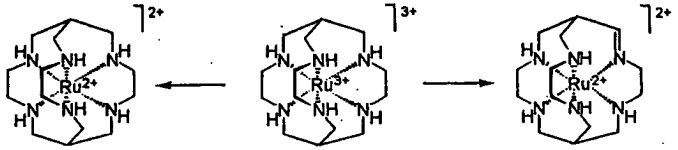



**Scheme 71**



oxidants [168]. Demetallation of the $[Co(capten)]^{3+}$ cation also made it possible to synthesize a $[Ru(capten)]^{2+}$ $N_3S_3$-sarcophaginate by interaction of a free ligand with $[Ru(DMF)_6]^{2+}$ solvato-complex.

The corresponding clathrochelate ruthenium(III) complexes have not been isolated because of spontaneous oxidation of the ligand with the central metal ion, whereby ruthenium(II) sarcophaginate and its monoimine analogue were obtained [5, 169].



(50)

The complexes of nickel(II) and copper(II) ions with *sar*-$N_4S_2$ and *AMHsar*-$N_4S_2$ ligands, respectively, have been produced from the free ligands and corresponding perchlorate salts in methanol [170, 171].

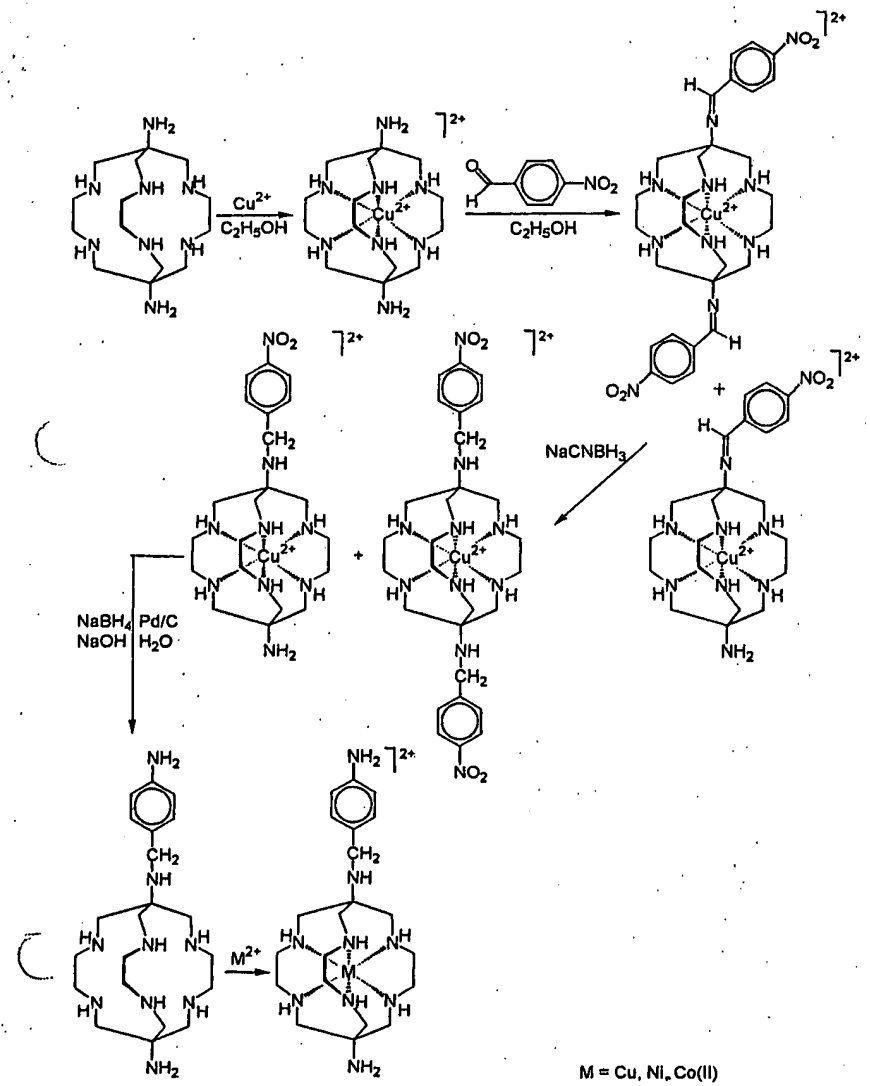
An analogous scheme has also been used for the synthesis of the nickel, copper, mercury, and zinc(II) diaminosarcophaginates [172-175], their N-methylated analogs [173], and simplest $[Hg(sar)](ClO_4)_2$ and $[Ni(sar)](ClO_4)_2$ sarcophaginates [174, 176].

One should take notice of an unusual $Co^{3+}$ ion extrusion procedure from the $[Co(diAMHsar)]^{5+}$ cage using an 8-hydroxyquinoline that was described in Ref. 177. The resulting ligand readily encapsulated nickel and copper(II) ions to produce octahedral complexes.

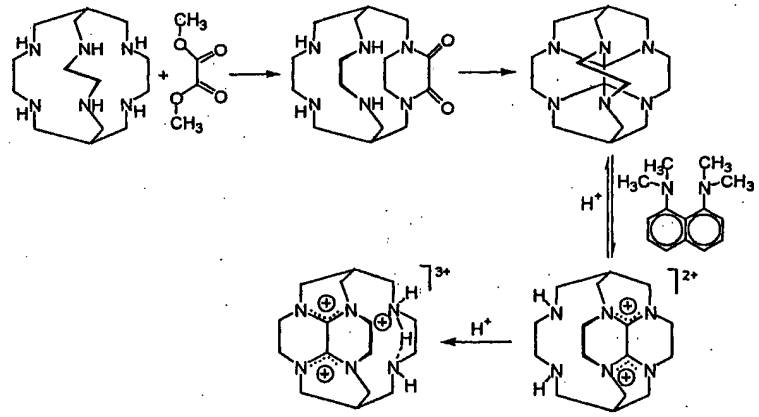
The copper(II) diaminosarcophaginate underwent condensation with 4-nitrobenzaldehyde to give nitrobenzylimine and bis-nitrobenzylimine sarcophaginates, which were reduced with a cyanoborohydride ion to corresponding saturated copper(II) clathrochelates. The copper(II) nitrobenzyldiaminosarcophaginate isolated underwent a reductive demetallation with $NaBH_4$ in the presence of palladium on activated charcoal under basic conditions. The resulting free aminobenzyldiaminosarcophagine *sarAr* ligand readily formed complexes with copper, nickel, and cobalt(II) ions (Scheme 72) [175].

Numerous magnesium(II), manganese(II), iron(II, III), silver(II), gallium(III), vanadium(III), and indium(III) sarcophaginates and diaminosarcophaginates are synthesized and structurally characterized [4, 178].

Manganese(II) $Mn(sar)](ClO_2)_4$, and $[Mn(diAMHsar)](NO_3)_4 \cdot H_2O$ sarcophaginates arose from the manganese(II) acetate and the




**Scheme 72**

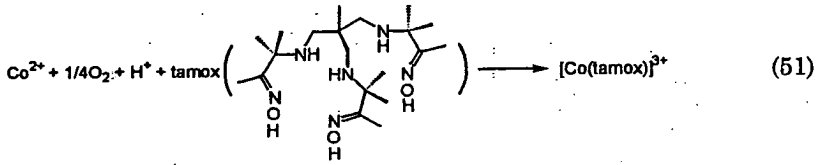


**Scheme 73**

corresponding free ligands in the absence of oxidant. The electrochemical and chemical oxidation of these complexes resulted in manganese(III) $[Mn(sar)](CF_3SO_3)_3$, $[Mn(sar)](NO_3)_3 \cdot 0.5H_2O$, and $[Mn(diAMHsar)](NO_3)_5 \cdot 2H_2O$ clathrochelates [179, 180].

The first step on the way to the synthesis of the so-called "superclathrochelates" containing a second shell, which reinforces the clathrochelate framework and completely excludes any possibility of metal ion extrusion without clathrochelate ligand destruction, is described in Ref. 181. The interaction of the simplest free sarcophagine with dimethyoxalate in methanol at room temperature resulted in the formation of the ethanosarcophagine. The protonation of ethanosarcophagine involving the splitting of two C–N bonds first led reversibly to the formation of an oxamidinium salt with nonprotonated amino groups and then irreversibly to the formation of a sarcophagine trication (Scheme 73) [181].

Hexadentate trioximetriamine compounds proved to possess properties intermediate between those of macrobicyclic trisdioximates and sarcophaginates. The hexadentate *tamox* ligand arises from the reaction of the corresponding polyamine with 2-chlor-2-methyl-3-nitrosobutane [182]:




(51)

The interaction of *tamox* ligand with $Co^{2+}$ ions in the presence of air oxygen led to the formation of $[Co(tamox)]Cl(ClO_4)_2 \cdot H_2O$ and $[Co(tamox–H)]Cl_2 \cdot 3H_2O$ complexes. These compounds appear to be promising for the synthesis of the corresponding clathrochelate complexes.

Methods for the synthesis of sarcophaginates and sepulchrates based on redox and photochemical reactions are discussed in Chapter 5.

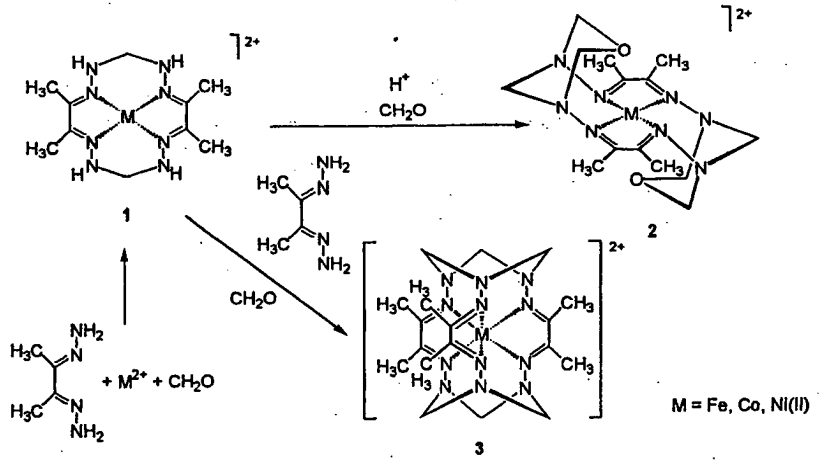
## 2.4 SYNTHESIS OF POLYENE AND OTHER TYPES OF CLATHROCHELATE COMPLEXES

The methods for the preparation of the clathrochelate complexes discussed in this section are, in most cases, similar to those for the macrocyclic compounds described in detail in Refs. 7, 11, 14, 15 and 17. In contrast to clathrochelates of other types, they are prepared largely *via* interaction between a preformed clathrochelate ligand and the appropriate metal salt. In other cases, the synthesis of these clathrochelates occurs *via* either template encapsulation or rearrangement from square-planar complexes (Scheme 74).

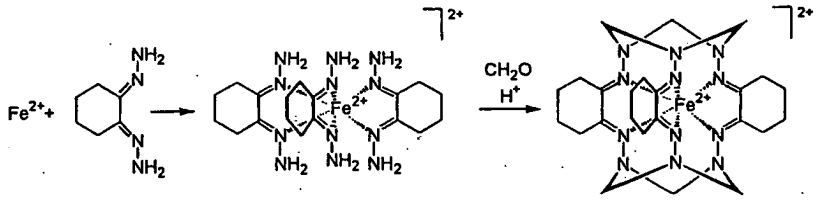
The condensation of butanedione-2,3-dihydrazone with formaldehyde on a metal ion ($Fe^{2+}$, $Co^{2+}$ and $Ni^{2+}$) matrix (Scheme 74), performed by Goedken and Peng, led to the formation of clathrochelate $[M(thz)](BF_4)_2$ complexes. Direct reaction between the three components proved to be efficient only with iron(II) ion [183]. Therefore, nickel, cobalt, and iron(II) tris-dihydrazonates were preliminarily synthesized. It was noted that even when the reaction was carried out under nitrogen and cobalt(II) tris-dihydrazonate was used as the starting material, only cobalt(III) clathrochelate could be isolated from the reaction mixture. Its reduction with anhydrous hydrazine yielded cobalt(II) clathrochelate [95, 183].

In the case of cyclohexanedione-1.2-dihydrazone, the macrobicyclic dihydrazonate formation proceeded on the template $Fe^{2+}$ ion more






**Scheme 74**




**Scheme 75**

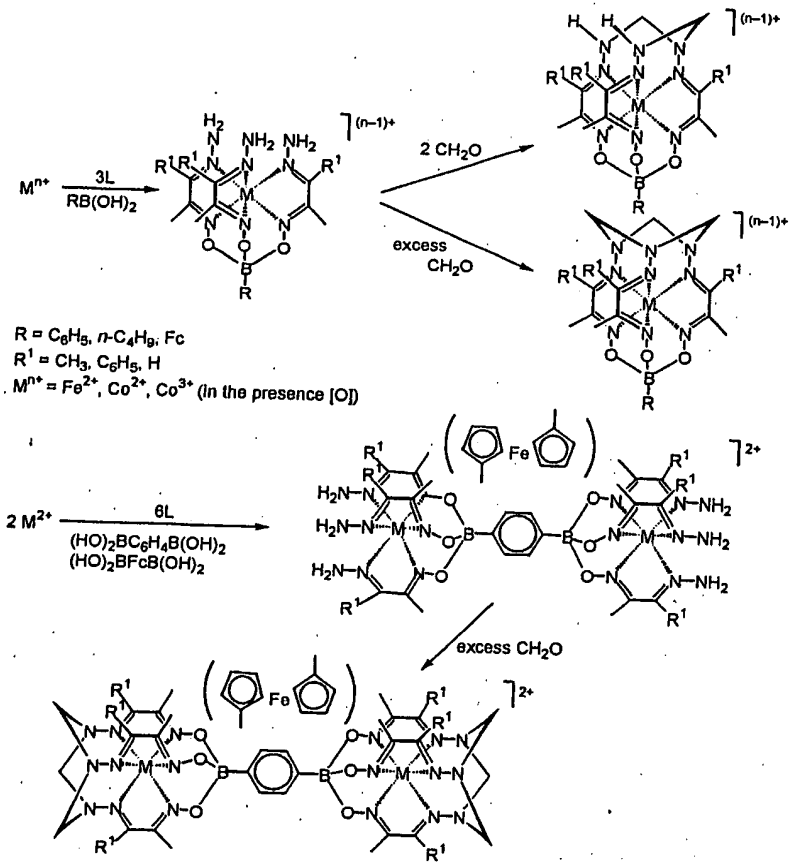
efficiently compared with the formation of butanedione-2,3-dihydrazone clathrochelate (Scheme 75) [184].

Goedken and Peng's idea to employ the reaction between the amino groups, bound to the metal ion, and formaldehyde for the synthesis of clathrochelates proved to be beneficial. It has served as a basis for later studies of Sargeson and coworkers on the synthesis of sepulchrates and sarcophaginates.

When α-oximehydrazones were used as the chelating agents, researches succeeded in the synthesis of mono- and bis-clathrochelate iron and cobalt(II) oximehydrazonates [185-187]. At the first stage, mono- and bis-semiclathrochelate iron and cobalt(II) complexes were isolated by a cross-linking with phenylboronic or ferrocenylboronic acids, and with benzene-1,4-diboronic or 1,1'-ferrocenyldiboronic acids,

respectively. A subsequent cyclization of these semiclathrochelates with an excess of formaldehyde in the presence of catalytic amounts of $HBF_4$ or $HPF_6$ led to the formation of clathrochelates. The interaction of the equimolar quantities of formaldehyde and semiclathrochelate complexes resulted in partially cross-linked compounds with two methylene units (Scheme 76).

With the *n*-butylboronic acid, a semiclathrochelate intermediate product was not pre-isolated and the clathrochelate complex was produced from a template reaction [185].




**Scheme 76**

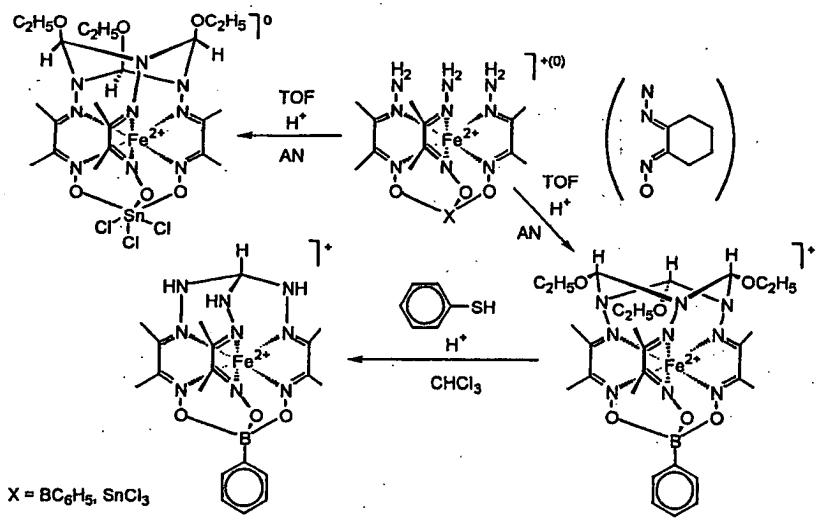


The above-mentioned semiclathrochelate oximehydrazonates are visualized as highly intriguing compounds for capping since their geometry may be varied over a wide range from trigonal prism to trigonal antiprism by changing the first capping fragment, in particular, in passing from a boron- to a tin-containing capping group. In this manner one specifies the geometry of the resulting clathrochelates and the orientation of substituents in the second capping fragment [188].

Syntheses of the overwhelming majority of clathrochelate complexes have proceeded *via* an intermediate nonmacrocyclic compound containing spatially oriented oxime, amine, or hydrazonate nitrogen atoms in the triangular bases of the coordination polyhedron. The trifunctional reagents are evidently thought to be the most natural capping agents. To form a tripod apical fragment in the syntheses of the most thoroughly studied complexes, such as sarcophaginates, methyl groups with C–H acidic properties (e.g., in nitromethane or cobalt pyruvate) or active hydrogen atoms of Group 5 hydride compounds (ammonia, phosphine, or arsine) interacting with intermediate amine complexes in the presence of aldehyde (mainly formaldehyde forms methylene bridging units between the apical and the coordinated nitrogen atoms) have been used (see Section 2.3). Condensation reactions of tripod amines or imines with activated and oriented carbonyl groups have been used in the syntheses of mono- and binuclear azomethine clathrochelates (see below). Finally, the template condensation of *d*-metal tris-dioximates with Lewis acids produced a tripod capping fragment formed by the capping atom and three oxygen atoms (see Section 2.1).

As mentioned above, with bifunctional reagents such as formaldehyde, the oriented hydrazonate amino groups react in the plane of the triangular base to produce 1,3,5-triazacyclohexane ring. It is clear that the formation of the macrobicyclic structure requires bi- and trifunctional agents exhibiting high activity toward reactive groups, e.g., trichloroacetaldehyde (TAA) or triethyl orthoformate (TOF).

Iron and cobalt (III) tris-dioximates and tris-ethylenediaminates have not been capped by TOF and TAA. The reaction of iron(II) tris-diacetyldihydrazonate with TOF has yielded no tripod capping fragment. However, the condensation of three apical hydrazonate amino groups and three TOF molecules gave a 1,3,5-triazacyclohexane fragment with statistical orientation of substituents (hydrogen atoms and ethoxy groups) relative to the ring. The use of



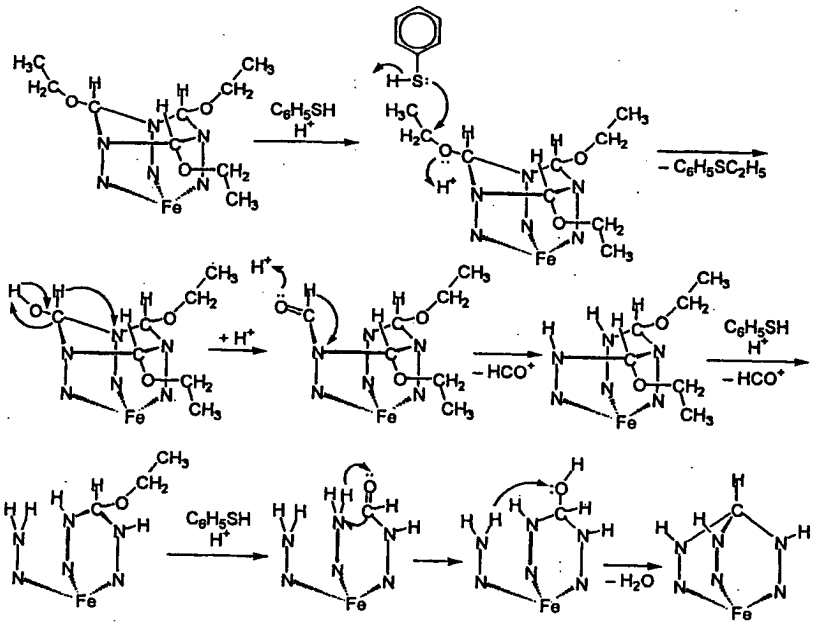

**Scheme 77**

TOF in equimolar amounts also failed to produce the tripod capping fragment [188].

Attempts to employ tris-oximehydrazonate complexes with *HDXO* and *HCXO* ligands proved to be successful. The $H^+$-catalyzed interaction of preliminarily obtained boron- and tin-capped semiclathrochelates **1** and **2** with excess TOF resulted in only one isomer (Scheme 77) with *cis* or *trans* orientation of the ethoxy groups and the semiclathrochelate fragment relative to the 1,3,5-triazacyclohexane ring [188].

Clathrochelate complexes resulting from reaction with TOF involving ethoxy groups are thought to be highly promising compounds for functionalization and for the synthesis of novel clathrochelates with improved properties. One of the most interesting types of modification reactions of the sarcophaginates proved to be intramolecular rearrangement, e.g., a partial rearrangement of the regular sarcophagine framework to yield a macrobicyclic ligand with a contracted cavity during nitrosation of cobalt(III) aminosarcophaginates (see Section 2.3). The $H^+$-catalyzed intramolecular condensation of boron-capped complexes was also observed. This reaction requires prolonged refluxing and occurs in the presence of





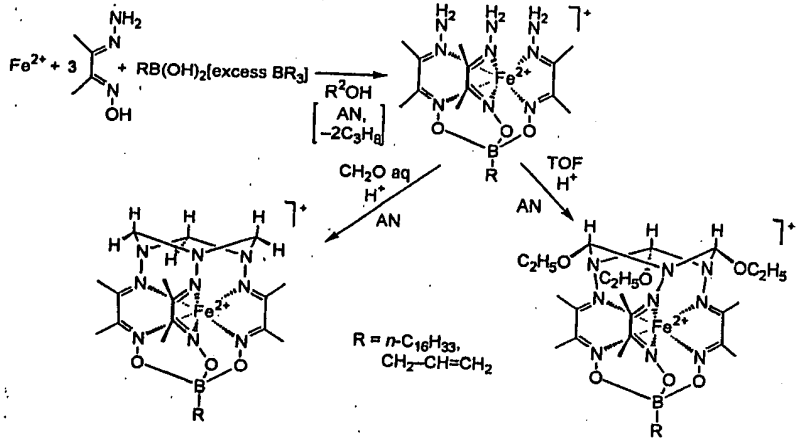

**Scheme 78**

thiophenol, which binds the ethoxy-containing fragments that are detached in the course of the reaction.

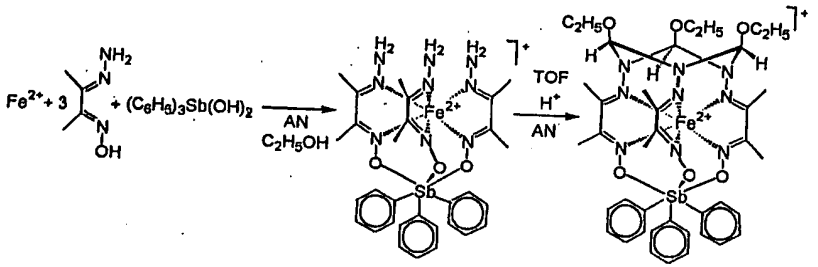
The mechanism of this intramolecular condensation resulting in a tripodal capping fragment is represented in Scheme 78. The alkyl ethers can be smoothly cleaved by a thiophenol derivative in the presence of a strong acid. The reaction "push-pull" mechanism involves the cooperative $H^+$ ion addition to the ether oxygen atom and the nucleophilic attack of sulphur on the ethyl group. As a result, the transformation of two amino fragments into amide fragments occurs. The amide fragments detach of formyl groups, and the intramolecular condensation with the third amide fragment results in a tripodal cap.

The apical functionalized oximehydrazonate clathrochelates were also obtained stepwise from initial semiclathrochelate precursors followed by $H^+$-catalyzed condensation with an excess of formaldehyde or TOF (Scheme 79) [67].

The first antimony-capped oximehydrazonate semiclathrochelate was obtained by condensation of $FeCl_2 \cdot 4H_2O$ and diacetylmonooxime




**Scheme 79**

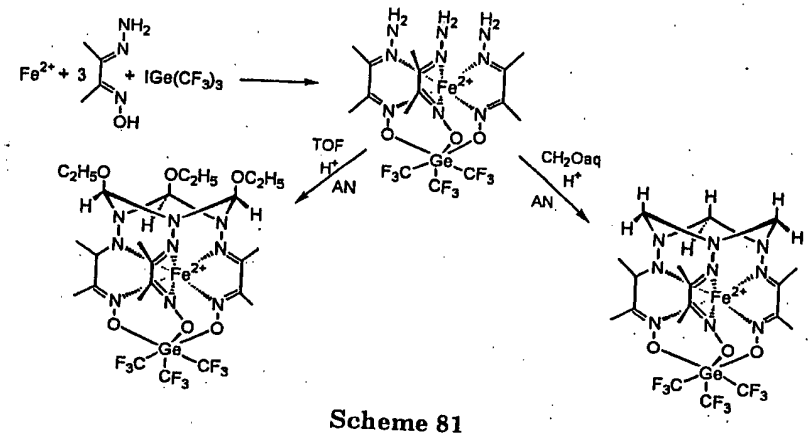



**Scheme 80**

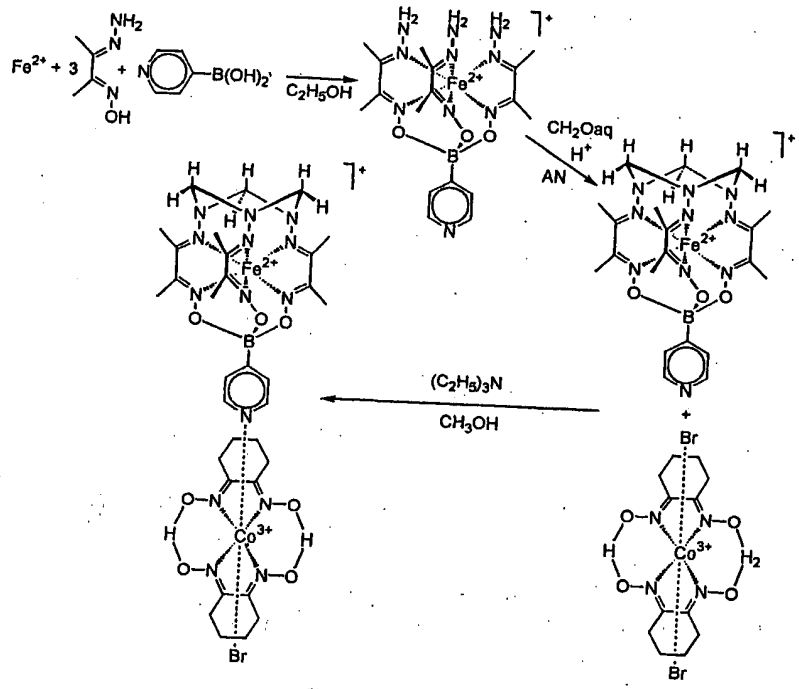
hydrazone with $(C_6H_5)_3Sb(OH)_2$ in acetonitrile / ethanol mixture (Scheme 80). $H^+$-ion-catalysed reaction of semiclathrochelate in acetonitrile with fivefold excess of TOF resulted in the desired antimony-capped clathrochelate [74].

The condensation of three *HDXO* molecules with $IGe(CF_3)_3$ on the iron(II) ion as template gave of $FeDXO_3(Ge(CF_3)_3)$ semiclathrochelate in high yield, even in the absence of base neutralizing the $H^+$ ions. In this case the *HDXO* ligand itself proved to be a base. The semiclathrochelate formed underwent $H^+$-ion-catalysed condensation with formaldehyde and TOF, resulting to the first clathrochelate germanium-capped oximehydrazonates with a capping 1,3,5-triazacyclohexane group (Scheme 81) [73].






**Scheme 81**




**Scheme 82**

Apically functionalized clathrochelate iron(II) oximehydrazonate with an appended pyridyl and its complex with $[Co(H_2Nx)(HNx)]Br_2$ cobaloxime were prepared by Scheme 82 [189].

An alternative pathway for the synthesis of bis-clathrochelates that was proposed in Ref. 75, can be realized with bis-capping agents, which are apt to accept an additional two electron pairs, and if the electron-donor groups of $C_2$-nonsymmetric ligands, participating in the capping, demonstrate essentially different chemical properties. Scheme 83 shows a pathway for the synthesis of an oximehydrazonate iron(II) bis-clathrochelate starting from *HDXO* ligand, the oxime and hydrazonate groups of which displayed appreciably different chemical properties. With bis-capping germanium(IV) tetraethoxide, oximehydrazonate iron(II) bis-semiclathrochelate was presumably formed at the first stage. A further $H^+$-catalyzed macrocyclization through the hydrazonate groups was implemented with triethyl orthoformate as described above [75].

For an efficient synthesis of clathrochelates, the orientation of active carbonyl-containing (e.g., acylchloride) groups in their reactions with amines has been used alongside that of coordinated amino groups in their reactions with carbonyl-containing cross-linking agents. A macrobicyclic ruthenium(II) tris-diiminate was prepared [190] *via* template cross-linking of nonmacrocyclic precursor with tripodal amine (Scheme 84).

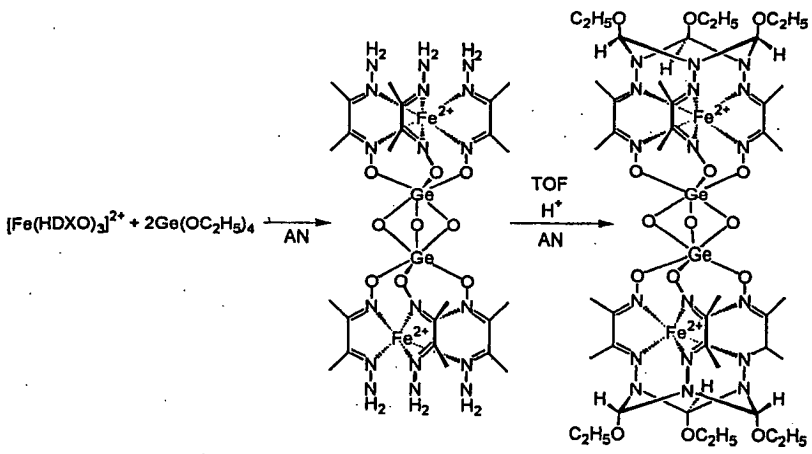
The analogous iron(II) complex was isolated [191] by interaction of an iron(II) salt with the *tabpy* ligand preliminarily obtained by Scheme 85.

A clathrochelate binucleating *trom* ligand was synthesized *via* two-step condensation of the tripodal *tren* amine with 2-oxy-5-methylisophthalaldehyde (Scheme 86) [192].

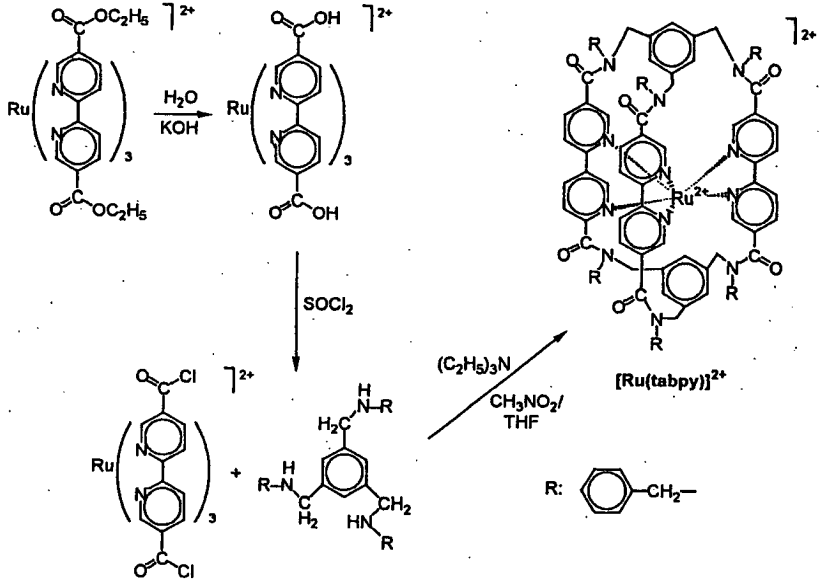
Homobinuclear macrobicyclic copper, cobalt, and iron(II) complexes and a heteronuclear iron(II)/cobalt(II) clathrochelate of the $[M_1M_2(trom)]^+$ type arise from interaction of a sodium complex of *trom* ligand with the corresponding metal salts.

Polynuclear iron(II) and cobalt(III) oximehydrazonates have arisen from the template macrocyclization of the initial nonmacrocyclic tris-complexes with polydentate ligands resulting from the condensation of the corresponding diketones and their monooximes with hydrazine [193]. The tris-complexes formed have

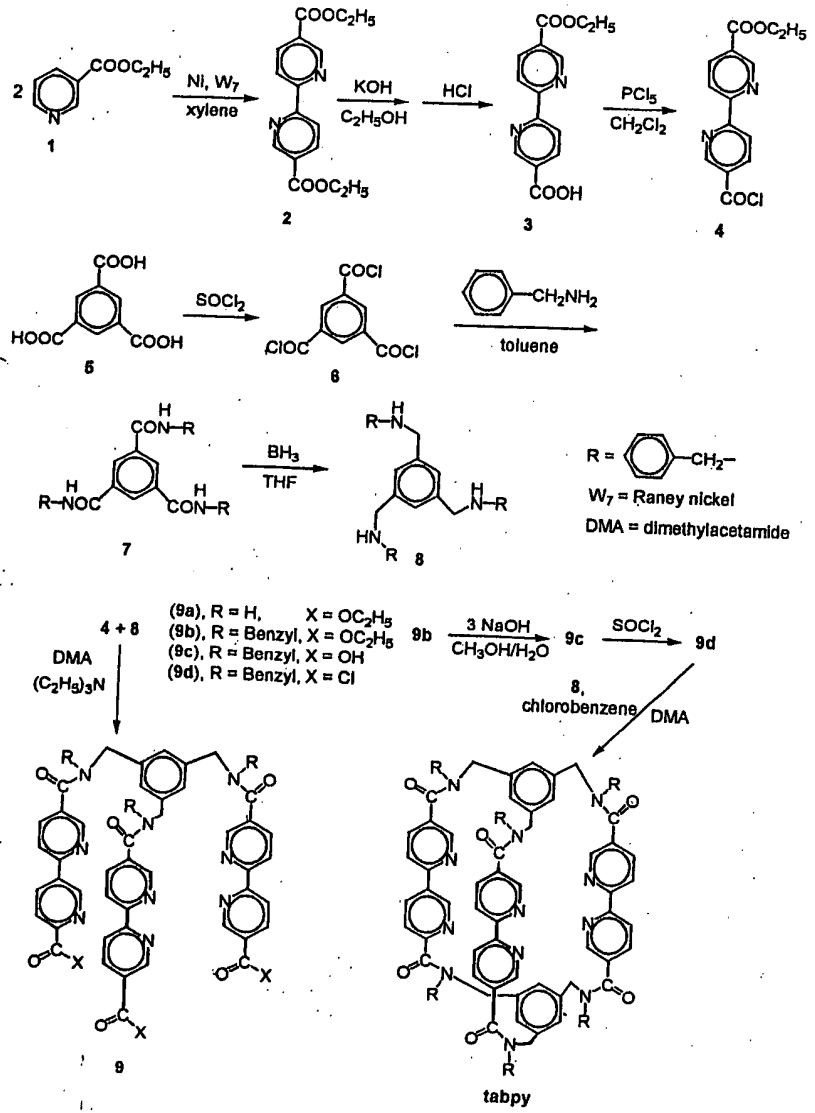





**Scheme 83**

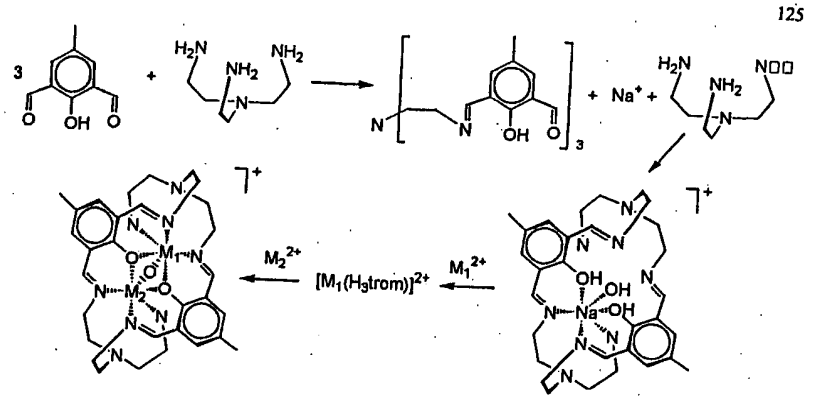



**Scheme 84**

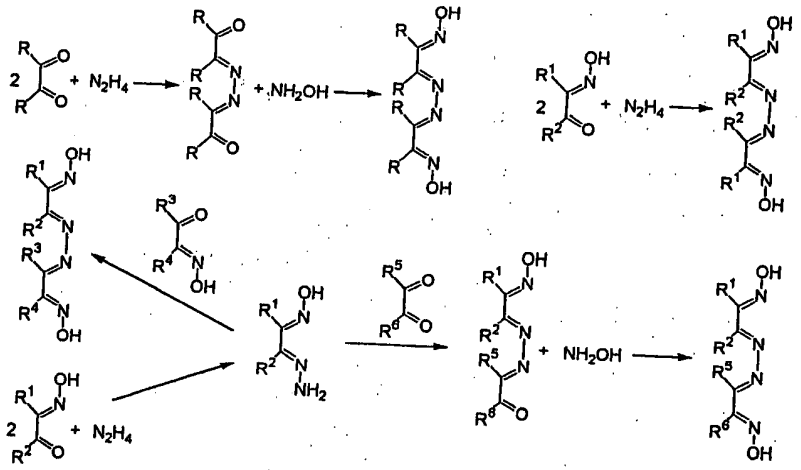



Scheme 85






Scheme 86




Scheme 87

interacted with Lewis acids *via* oxime-containing fragments to give clathrochelate complexes.

The initial oximehydrazonate ligands were prepared by the methods represented in Scheme 87. Different strategies employed in the synthesis of these compounds permit one to prepare ligands of a tailor-made structure by varying the diketones, their monooximes, the molar ratios of reactants, and the reaction sequence. In addition,

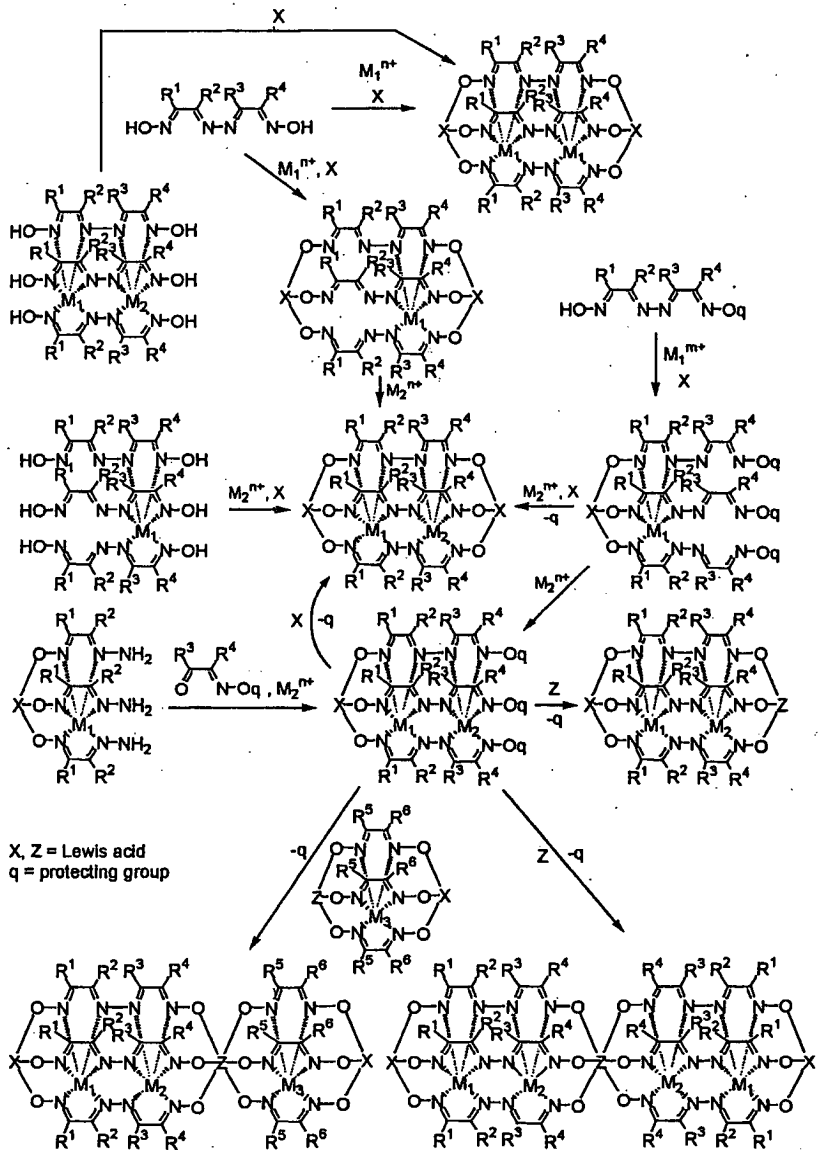
oximehydrazonate ligands can be prepared from fragments by a template reaction on a metal ion, for instance, by building up mononuclear tris-complexes to binuclear ones [193].

Binuclear clathrochelate iron(II) oximehydrazonates may be synthesized by the main methods used for the synthesis of macrobicycles of this type proposed for clathrochelate tris-dioximates: by a direct template reaction on a metal ion; the cross-linking of initial nonmacrocyclic complexes; a cross-linking group exchange reaction; and a ligand modification reaction. The template condensation of a mononuclear complex to a binuclear one followed by the encapsulation of another metal ion and capping reaction may be also used for the preparation of these compounds. The main methods for the synthesis of these complexes are shown in Scheme 88 [193].

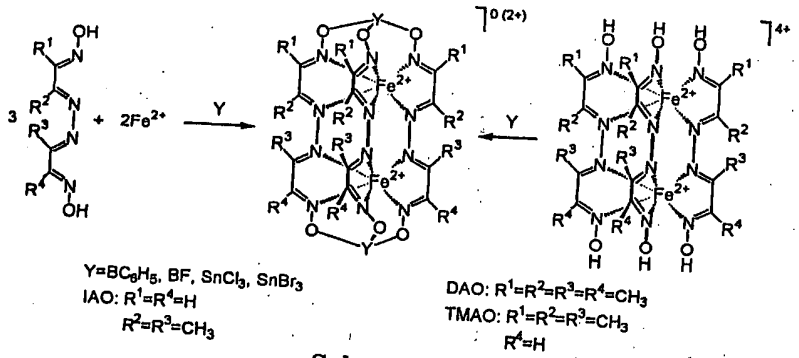
With tetradentate ligands, the direct template reaction is accompanied by a large number of side reactions, which substantially decreases the interest in this commonly employed method of synthesis. Therefore, cross-linking of tris-complexes and condensation reactions of lacunar compounds have been mainly used to prepare the complexes. In the case of $C_2$-nonsymmetric ligands, the latter method allows one of the steric isomers (*fac* or *mer*) instead of their mixture to be obtained, provided that presynthesized ligands are utilized. The fact that the second metal ion can be encapsulated by a clathrochelate with a vacant cavity is due to the reversibility of a capping reaction with Lewis acids. In appropriate conditions a cross-linking fragment reversibly dissociates to yield a semiclathrochelate product with a vacant cavity. The latter can encapsulate a second metal ion with the subsequent reversible addition of the capping fragment. It is obvious that with a proper metal ion, the stability of the resultant binuclear complex is substantially higher than that of the initial mononuclear complex, which leads to the equilibrium shift toward the binuclear clathrochelate.

When $Fe^{2+}$ ions interact with oximehydrazonates in solution, a mixture of complexes is formed by a stepwise complexation. In the case of the *$H_2$DAO* and *$H_2$TMAO* ligands (L), the $[Fe_2L_3](BF_4)_4$ and $[FeL_3](BF_4)_2$ complexes were isolated. The mononuclear compound disproportionates quickly to form a binuclear complex and the parent ligand. The $Fe^{2+}$ ions interact with the *$H_2$IAO* ligand to form an insoluble polymeric complex, which, however, reacts with efficient cross-linking agents [193].






**Scheme 88**

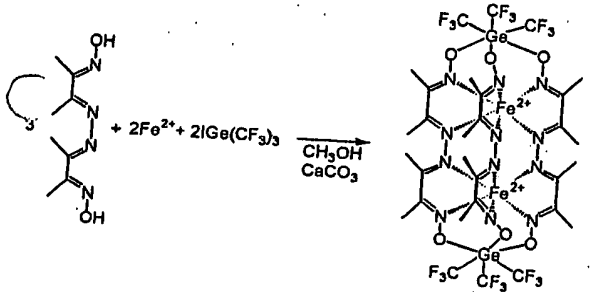



**Scheme 89**

Macrobicyclic binuclear iron(II) oximehydrazonates were synthesized by encapsulation of initial nonmacrocyclic tris-complexes with boron- and tin-containing Lewis acids and by direct template reactions on the $Fe^{2+}$ ion (Scheme 89).

The $[Fe(DAOBz)_3(BC_6H_5)](BF_4)$, $[Fe_2(DAOBz)_3(BC_6H_5)](BF_4)_3$, $[Fe(HDAOBz)_3](ClO_4)_2$ and $[Fe_2(HDAOBz)_3](ClO_4)_4$ complexes of the monobenzylated *HDAOBz* ligand were also isolated. This ligand allows one the stepwise preparation of clathrochelates with cross-linking groups of various types [193].

The binuclear germanium-capped clathrochelate $[Fe_2DAO_3(Ge(CF_3)_3)_2]$ oximehydrazonate was obtained by a template condensation of the tetradentate *H₂DAO* ligand with $IGe(CF_3)_3$ in an aqueous solution in the presence of $CaCO_3$ (Reaction 52). The resulting intramolecular macrobicyclic compound precipitated from the reaction mixture, and the equilibrium shift due to the formation of the solid allowed one to isolate this complex in a relatively high yield [73].

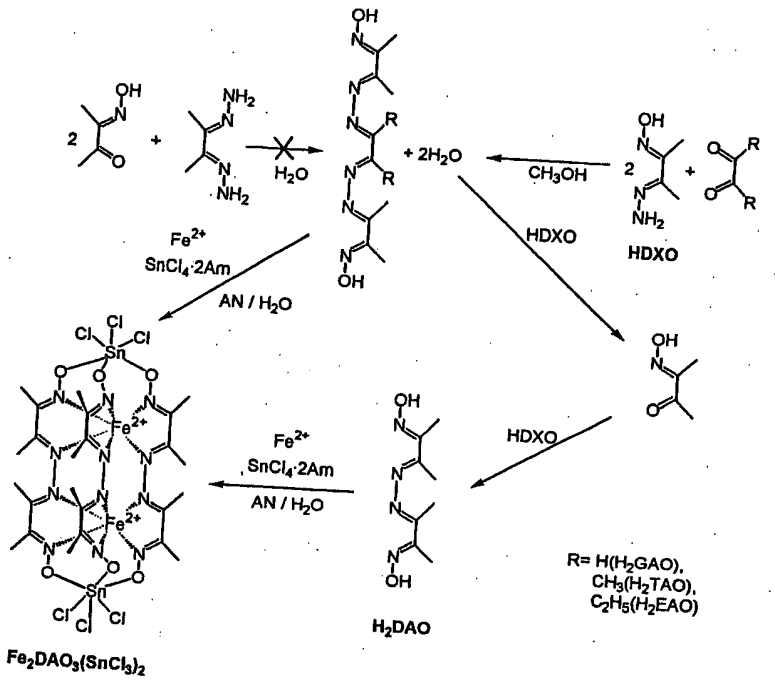



(52)



Potentially hexadentate tetraazinedioximate ligands were described in Ref. 194. The condensation of diacetyl monooxime with diacetyl dihydrazone in water (Scheme 90) initially proposed in literature for the synthesis of *H₂TAO* azineoxime has failed to give this compound: according to the $^1H$ and $^{13}C$ NMR data, the oximehydrazone resulting from 1:1 condensation is predominant in the reaction product mixture. A synthetic route for potentially hexadentate *H₂TAO*, *H₂EAO*, and *H₂GAO* azineoximes based on the condensation of diacetyl monooxime hydrazone with the corresponding active α-dicarbonyl compound (diacetyl, 3,4-butandione and glyoxal, respectively) in methanol was more successful (Scheme 90) [194].

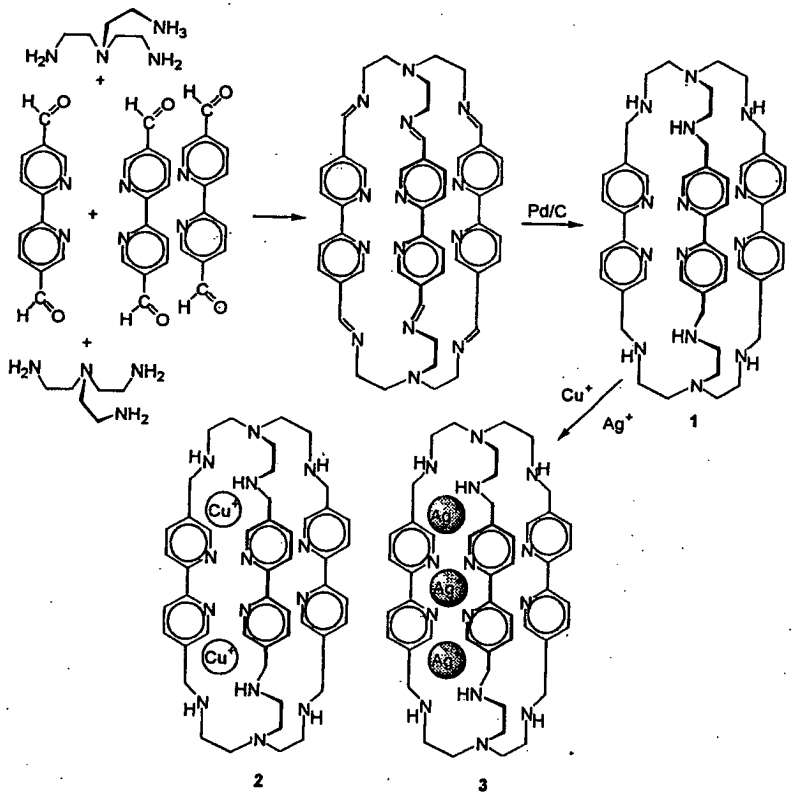
The reaction of the resultant azineoximes with $Fe^{2+}$ ions in the presence of cross-linking agents (Lewis acids, in particular $SnCl_4$) proceeded by an unexpected pathway. In all cases, even in aprotic




**Scheme 90**

media (e.g., in dry acetonitrile), instead of the expected trinuclear $[Fe_3L_3(SnCl_3)_2]^{2+}$ clathrochelates (where L is $TAO^{2-}$, $EAO^{2-}$, $GAO^{2-}$ dianions), only one clathrochelate $Fe_2DAO_3(SnCl_3)_2$ complex in an essential yield (*ca* 20%) was obtained (Scheme 90). The initial azineoximes apparently disproportionated in the course of the reaction, "kicking out" the central fragment to form a highly stable and poorly soluble binuclear clathrochelate that precipitated from the reaction mixture [194].

The one-stage condensation of *tren* with 5,5'-diformyl-2,2'-bipyridine made it possible to also obtain the macrobicyclic Schiff base, whose hydrogenation on the palladium catalyst yielded the clathrochelate tris-bipyridine *tranbpy* ligand 1 (Scheme 91) [195].




**Scheme 91**

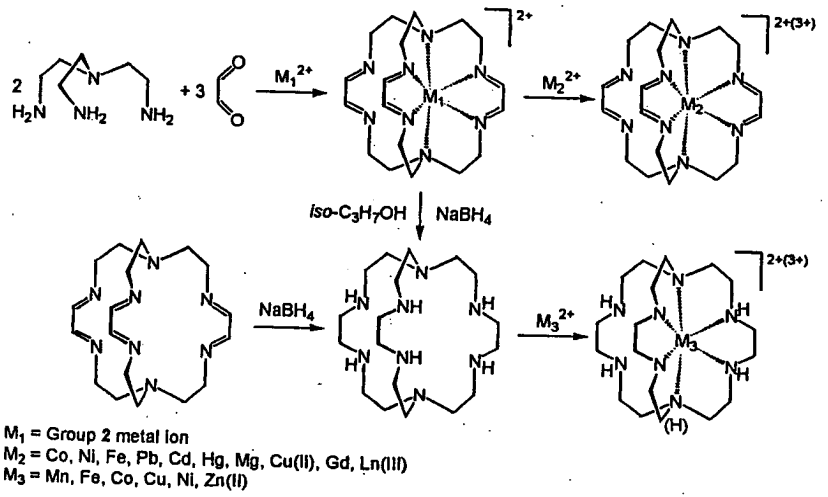


The interaction of *tranbpy* ligand with an excess of $[CuAN_4](BF_4)$ and $AgBF_4$ led to the formation of a binuclear $[Cu_2(tranbpy)](BF_4)_2$ (2) and a trinuclear clathrochelate $[Ag_3(tranbpy)](BF_4)_3$ (3) compounds, as well as allowed one to isolate the heteroronuclear $Cu^I$–$Ag^I$–$Cu^I$ complex.

A new type of octaazamacrobicyclic Schiff bases was synthesized in high yields *via* a template condensation on Group 2 metal ions in ethanol at 40–50°C (Scheme 92) [196]. The resultant kinetically labile complexes readily transmetallize when reacted with transition metal (cobalt, nickel, iron, copper(II)) salts to form the corresponding mononuclear $[M(imBT)]X_2$ complexes (where X is $BF_4^-$ and $ClO_4^-$).

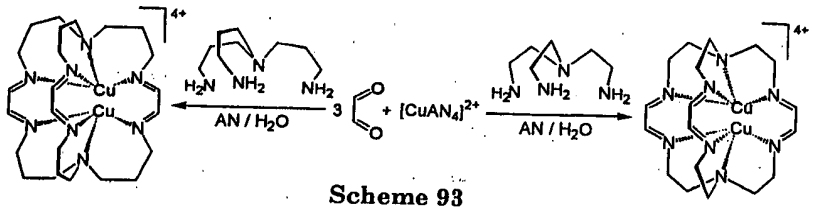
With an excess of $[CuAN_4](ClO_4)_2$, the first binuclear compound with a possibly delocalized bond of Cu(I)/Cu(II) was also prepared [197]. A detailed template synthesis of the binuclear copper(II) complexes of macrobicyclic *imBT* ligand with a regular cavity and an *imbistrpn* ligand with an expanded cavity (Scheme 93) is described in Ref. 198.

The isolated compounds of transition metals are kinetically inert. The interaction between $[Co(imBT)]^{2+}$ cation and an aqueous solution of NaCN leaves no $Co(CN)_2$ precipitate within several weeks. Irrespective [196], the clathrochelate *imBT* ligand was obtained *via* a




$M_1$ = Group 2 metal Ion
$M_2$ = Co, Ni, Fe, Pb, Cd, Hg, Mg, Cu(II), Gd, Ln(III)
$M_3$ = Mn, Fe, Co, Cu, Ni, Zn(II)

**Scheme 92**



Scheme 93

template reaction in the presence of $Rb^+$ and $Cs^+$ ions in methanol at 50°C (yield *ca* 60%) [199].

A detailed procedure for the synthesis of a free *imBT* ligand by the slow addition of aqueous glyoxal to *tren* solution in *iso*-propanol is described in Ref. 200. The free ligand obtained readily reacted with lanthanum and gadolinium(III) ions in an acetonitrile-chloroform mixture [201] and with lead, cadmium, and mercury(II) salts in acetonitrile-ethanol medium [202].

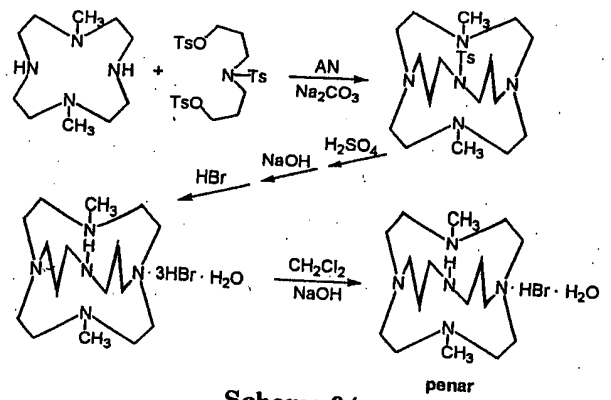
The reduction of *imBT* ligand with $NaBH_4$ in methanol led to the formation of a saturated octaazamacrocyclic *amBT* ligand that forms binuclear complexes with zinc(II) and copper(II) [199] and mononuclear clathrochelates with manganese, iron, cobalt, nickel, and zinc(II) [203] by treatment of the free ligand with the corresponding metal ion salts.

The cobalt(II) ion has been encapsulated with both neutral and protonated *amBT* ligand forms. In the case of nickel and zinc(II) ions, complexes with the sole protonated ligand form were obtained [203].

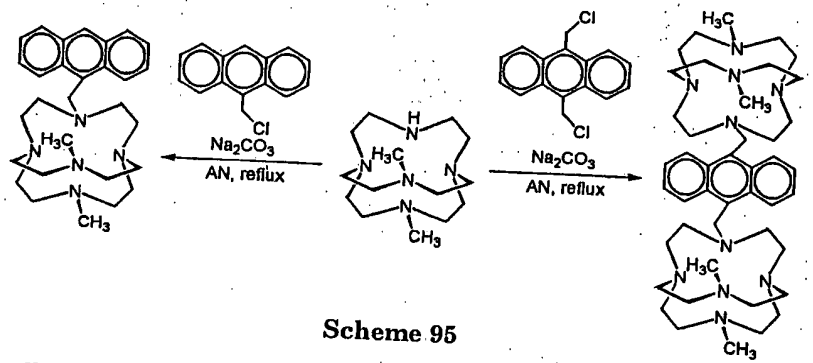
With pentaazamacrobicyclic clathrochelates, not only the nitrogen atoms of the side units but also capping apical nitrogen atoms take part in the coordination. Synthesis of such complexes was performed by interaction of the presynthesized macrobicyclic ligand (Scheme 94) with copper, zinc, cobalt, and nickel(II) perchlorates in boiling methanol [204].

The anthracene-functionalized $N_5$-cages have been obtained by two different procedures [205]: first, starting from the initial pentaazaclathrochelate precursor by condensation with mono- or dichloride anthracene derivatives to yield mono- and bis-clathrochelates, respectively (by Scheme 95 in the case of ethylene chains in the capping groups); and second, starting from the tetraazamacrocycle, containing two secondary amino groups in the *trans* position, by condensation with a protected diol derivative by the





Scheme 94



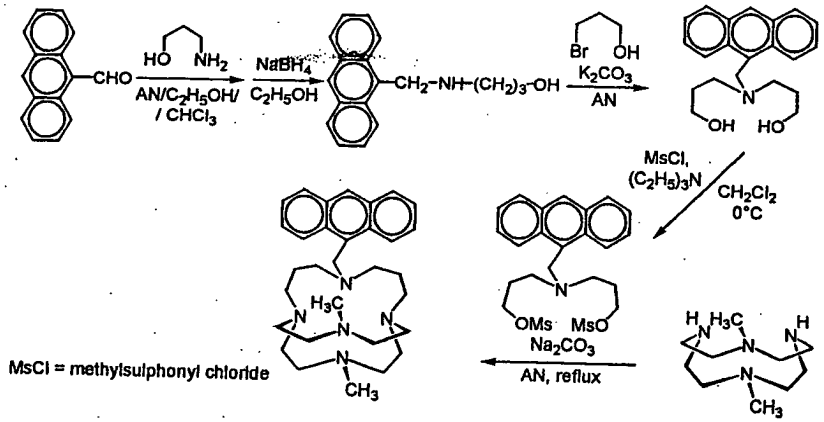
Scheme 95

well-known synthetic procedure from crown ether chemistry (Scheme 96, in the case of propylene chains in the capping groups).

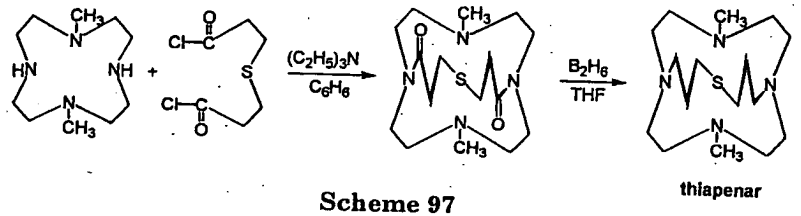
The anthracene-functionalized $N_5$-cage ligands readily reacted with an excess of LiOH in methanol to form complexes with an encapsulated $Li^+$ ion that are very soluble in organic solvents [205].

The use of 3,3'-thiodipropionicacylchloride instead of bis-(3-tosyloxy-propyl)tosylamine in the first step led to the formation of a macrobicyclic $N_4S$-pentadentate ligand (Scheme 97).

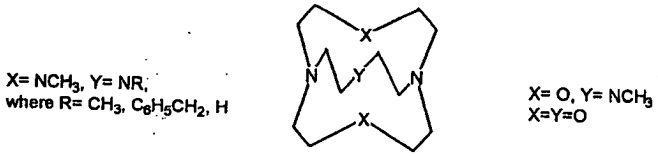
This ligand readily reacted with $Cu(ClO_4)_2$ in methanol to form a clathrochelate complex [206]. The macrobicyclic *mepenar* ligand with *N*-methylated ribbed fragments was obtained starting from bis-(3-tosyloxypropyl)methylamine. This ligand formed complexes with $Li^+$ ions (upon refluxing with 20-fold excess LiOH in ethanol),




**Scheme 96**




**Scheme 97**

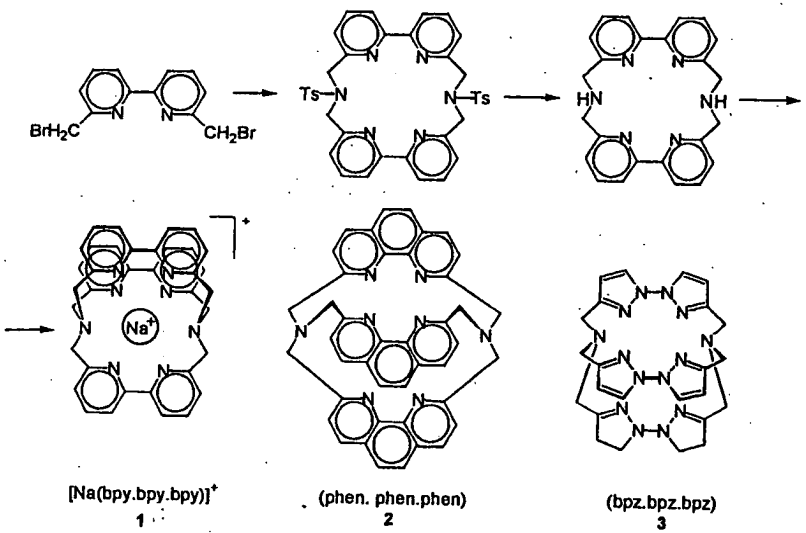



**Scheme 98**

$Cu^{2+}$ ions (*via* interaction with $Cu(ClO_4)_2 \cdot 6H_2O$ at a molar ratio of 1:1), and $Zn^{2+}$ ions (upon refluxing with $ZnBr_2$ in acetonitrile at a molar ratio of 1:1). No reactions between the free $N_5$- and $N_4S$-macrobicyclic ligands and $Na^+$, $K^+$, $Al^{3+}$, $Be^{2+}$, or $Ni^{2+}$ ions have been revealed [207-209].

The synthesis of $N_5$-, $N_3O_2$- and $N_2O_3$-pentadentate macrobicyclic ligands (Scheme 98) with unusually high basicity of the nitrogen-





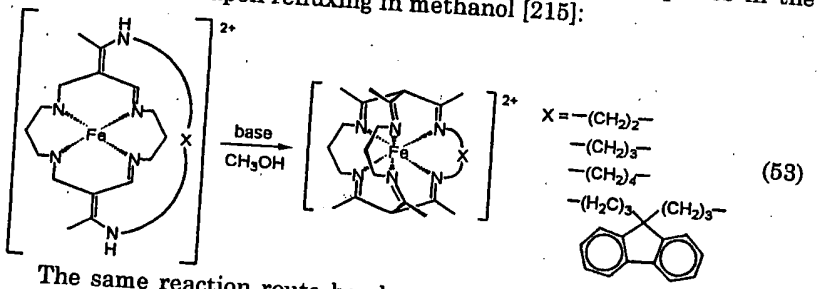

**Scheme 99**

containing fragment of the clathrochelate framework was realized in Ref. 210.

Macrobicyclic tris-bipyridinate **1** and tris-phenanthrolinate **2** as well as mixed *bpy.bpy.phen* ligand have also been prepared by a stepwise procedures (Scheme 99) involving the synthesis of a macrocyclic intermediate followed by its reaction with a capping agent on $Na^+$ ion [211]. The clathrochelate tris-bipyridinates and tris-phenanthrolinates of rare-earth elements have been produced by an exchange reaction between the corresponding sodium complexes and rare-earth metal nitrate or chloride upon prolonged heating in acetonitrile [212]. Interaction of the macrobicyclic tris-bipyridine ligand **1** (performed by a procedure slightly different from that proposed in [211]) with $RuDMSO_4Cl_2$ solvato-complex in aqueous ethanol resulted in the $[Ru(bpy.bpy.bpy)]Cl_2$ clathrochelate [213].

A more rigid tris-bipyrazole clathrochelate ligand **3** (Scheme 99) was synthesized by the scheme proposed for its bipyridine and phenanthroline analogs [214]. In contrast, the product isolated at the final stage was not a sodium clathrochelate, which makes it impossible to establish whether a template condensation on the $Na^+$ ion occurs.

Hexaene clathrochelate iron(II) complexes have been prepared by rearrangement of the preformed square-planar complexes in the presence of base upon refluxing in methanol [215]:




(53)

The same reaction route has been employed to isolate penta- and hexadentate semiclathrochelate iron(II) and cobalt(III) complexes [216, 217].



*Chapter 3*

# Spatial and electronic structure of clathrochelates

To gain information on the spatial and electronic structure of clathrochelates, researchers employ first, a direct method, X-ray crystallography, permitting them to obtain unambiguous data on the crystal and molecular structure of complexes, and second, indirect methods, such as IR, multynuclear NMR, UV-vis, and Mössbauer spectroscopies.

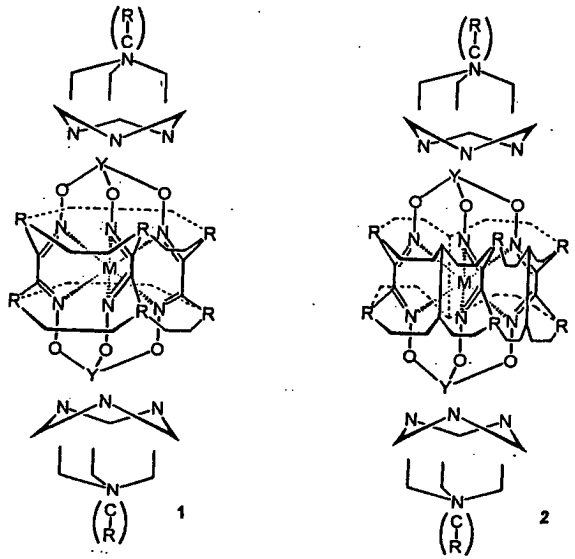
Since sarcophaginates and sepulchrates are relatively easy to crystallize, a great number of these compounds are studied by X-ray crystallography, which together with molecular geometry calculations makes it possible to establish their three-dimensional structures both in crystal and in solution. The optical activity of such clathrochelates enables one routinely to utilize circular dichroism measurements to investigate their structure. The spatial and electronic structures of sarcophaginates and sepulchrates are much more seldomly determined by alternative spectral techniques compared with clathrochelates of other types.

Phosphorus-containing tris-diimine *d*-metal complexes are isolated as ionic associates with a bulky inorganic $BF_4^-$ anion and readily crystallize. Therefore, monocrystals of these compounds, suitable for X-ray analysis, were obtained, and X-ray crystallography – the major method for determining their geometry – was applied to all complexes of this type. The subtle features of the electronic structure of macrobicyclic phosphorus-containing *d*-metal tris-diiminates have been examined by a variety of spectral methods and quantum-chemical calculations.

For macrobicyclic *d*-metal tris-dioximates, the X-ray crystallography analysis is performed least often. This is because the charge of the central metal atom in the majority of such compounds is balanced by that of the clathrochelate ligand, and crystals of the resulting intramolecular complexes are purely molecular. Alongside the structural peculiarities in the structure of such complexes, this

## 7.5. SUPERCLATHROCHELATE STRUCTURES

Compounds **1** and **2**, represented in Scheme 149, contain a second "shell" that completely excludes the extrusion of the metal ion without rupture of the clathrochelate framework and enforces a cage by additional covalent bonds. The first ligand of this type with a partially formed "secondary" structure was synthesized (see Chapter 2, Scheme 73). In this case, the encapsulated metal ion, exerting no influence on the number of physical characteristics of the complex such as solubility, volatility, and others, can be regarded only as the matrix that forms the macropolycyclic system [433].



**Scheme 149**



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